



Experimental Measurements of Particulate Matter Deliquescence and Crystallization Relative Humidity: Application in Heritage Climatology

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ABSTRACT

Climate and pollution can lead to materials weathering. In this study, an innovative method is employed to evaluate the hazard for heritage stone substrates induced by the synergic effect of particulate matter (PM) and climate. In this respect, two hazard indicators for stone materials were determined: the time of wetness and the number of dissolution and crystallization cycles. The two indicators were computed by coupling experimental measurements of the PM deliquescence and crystallization relative humidity with climatic data. For the first time, these indicators were estimated based on the PM hygroscopic properties, considering its whole hysteresis loop and its consequent hydration level.

The proposed method was applied to PM samples collected in the polluted Po Valley (Milan): the experimental measurements of both PM deliquescence and crystallization relative humidity were performed in an environmental-controlled chamber using an electrical conductivity method. The time of wetness and the number of dissolution and crystallization cycles were then calculated by coupling the PM deliquescence and crystallization relative humidity with climatic data of Milan over the last decade (2003–2013). Results point out that, depending on the seasons, different hazards were identified. In winter, high time of wetness ($89 \pm 11\%$) and low number of cycles (3 ± 3 cycles/month) were found. Conversely, summer was characterized by low time of wetness ($20 \pm 13\%$) and high number of cycles (11 ± 5 cycles/month). Interestingly, spring and fall resulted the most dangerous seasons for outdoor-exposed stones, since they presented both high time of wetness and number of cycles. Since the two indicators are calculated considering PM properties and climatic data, their values are site-specific, while the method used for their determination is of general application and it can be used for an efficient hazard assessment in a heritage climatology perspective.

Keywords: Time of wetness; Hygroscopicity; DRH; CRH; Particulate matter; Cultural heritage.

INTRODUCTION

The decay of outdoor-exposed stone materials may heavily depend on factors related to climate and pollution (Sabbioni, 1995; Bonazza *et al.*, 2009; Ghedini *et al.*, 2011; Urosevic *et al.*, 2012). In this respect, the strong correlation between climate and materials weathering has been recently highlighted with the concept of “heritage climatology” (Brimblecombe, 2010; Grossi *et al.*, 2011).

Particulate matter (PM) can cause damage to outdoor-exposed stone surfaces (Camuffo *et al.*, 1982; Grossi *et al.*, 2003; Ferm *et al.*, 2006). Recently, its role in materials-decay processes is receiving growing attention (together with NO_x and O_3) due to the decreasing concentrations of other

gas-phased acid pollutants such as SO_2 (Ferm *et al.*, 2005; Kucera *et al.*, 2007; Ghedini *et al.*, 2011; Urosevic *et al.*, 2012).

PM is a complex mixture of substances (Perrone *et al.*, 2012) and several studies highlighted the role of some single PM's components in specific stone-decay processes (Saiz-Jimenez *et al.*, 1993; Rodriguez-Navarro and Sebastian, 1996; Torfs *et al.*, 1997; Chabas *et al.*, 2000; Zanardini *et al.*, 2000; McAlister *et al.*, 2008; Stefanis *et al.*, 2009; Ozga *et al.*, 2011; Potgieter-Vermaak *et al.*, 2012). Nevertheless, few works have tried to assess the potential role of PM considering its comprehensive chemical-physics properties and its behaviour during climatic variations. The PM hygroscopicity could be one of the most relevant properties related to stone decay studies (Camuffo *et al.*, 1982; Camuffo, 1995; McAlister *et al.*, 2008); it can be described by two key-parameters: the deliquescence relative humidity (DRH) and the crystallization relative humidity (CRH). These are the relative humidity (RH) thresholds at which a phase change of the PM water-soluble fraction occurs: from solid to a

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saturated solution at DRH, and vice versa at CRH (Potukuchi and Wexler, 1995a, b; Martin, 2000; Speer *et al.*, 2003; Seinfeld and Pandis, 2006). In the case of atmospheric particles, or other similar complex systems, CRH is generally lower than DRH, thus generating a hysteresis loop in the hydration levels (Seinfeld and Pandis, 1998 and references therein; Martin, 2000; Martin *et al.*, 2003; Randriamiarisoa *et al.*, 2006; Ferrero *et al.*, 2013a, 2014).

DRH and CRH both depend on the whole PM chemical composition, which changes in time and space because of PM sources variability and atmospheric reactivity. These parameters may be different for PM from different sites and seasons and, with respect to each site-specific climatic condition, this may result in a different hazard for exposed stone materials.

Several indicators have been proposed in literature for the evaluation of the hazard for outdoor-exposed stone substrates. In this respect, some authors (Brimblecombe *et al.*, 2006; Bonazza *et al.*, 2009) have focused their attention on the time of wetness (TOW) that represent the time fraction during which liquid water could be present on a stone surface. Liquid water can trigger a large number of decay processes, such as solid-liquid reactions, acid attack, penetration of salts solutions in the porosity of materials and biofilms formation. Thus, the TOW describes the hazard that a stone could be exposed to because of “chemical” decay-mechanisms (Camuffo, 1995; Cardell-Fernandez *et al.*, 2002; Dohene, 2002).

Another indicator was introduced by Grossi *et al.* (2011) who focused their attention on the phase-transition events. They proposed the number of crystallization-dissolution cycles (Ncy) as a stone hazard indicator that describes the number of phase transitions (from solid to solution, and back to solid) of soluble stone contaminants due to ambient RH variations. As a consequence, Ncy indicates the hazard that a stone could be exposed to because of “mechanical” decay-mechanism due to the stress induced when crystallization occurs.

Thus, TOW and Ncy appear as promising indicators of the hazard for stone substrates, even if their quantification was conducted just using simplified approaches. Concerning TOW, for example, the wetting of surfaces was often assumed when RH was greater than 80% and temperature was greater than 0°C (Brimblecombe *et al.*, 2006; Bonazza *et al.*, 2009). With a different approach, Ponziani *et al.* (2012) used the Distance to Dew Point (DDP) index and the Kelvin equation to assess the condensation events frequency. As stated by Camuffo (1995) all these methods are valid for non-reactive surfaces, and the presence of contaminants may cause deviations from such a quite simple model.

A similar situation is present for the Ncy computation: most of the literature studies exploited the equilibrium humidity point of pure salts to assess the number of phase transitions in function of ambient RH variations (Doehne, 2002; Steiger, 2005; Grossi *et al.*, 2011). However, these studies mainly focused on the problem of salts contaminants derived from capillary rising damp, while in the case of PM, and its possible effects on stone surfaces, the whole hysteresis loop has to be considered (Ferrero *et al.*, 2014).

As a consequence, an accurate knowledge of both DRH

and CRH is required for an appropriate calculation of TOW and Ncy. This procedure allows proper assessment of the hazards for stone substrates considering the site-specific synergy between PM properties and climatic conditions.

This approach is of particular importance for such territories in which a large and heterogeneous amount of built heritage lies in a highly PM polluted environment. The Italian territory is a typical example of this situation, especially for what concerns the Po Valley: an European hot spot with one of the worst atmospheric PM pollution in Europe. This is due to the high density of anthropogenic PM sources, low mixing layer height, poor ventilation and secondary PM formation (Rodriguez *et al.*, 2007; Carbone *et al.*, 2010; Ferrero *et al.*, 2012). In the Po Valley the chemical composition of PM is strongly seasonally modulated by a variation within the ionic fraction from a nitrates-predominance in winter to a sulphates-predominance in summer (Sangiorgi *et al.*, 2011; Perrone *et al.*, 2012; Ferrero *et al.*, 2013; Perrone *et al.*, 2013). Thus, also the PM affinity for water changes with seasons.

Given the aforementioned state of the art on the heritage climatology approaches, this paper fills the gaps concerning the quantification of the hazard for heritage stone substrates due to the synergic effect of climate and atmospheric PM. With respect to this, a new method for the evaluation of two useful hazard indicators (TOW and Ncy) is proposed. This method is based on the measurements of the PM DRH and CRH that are applied to accurately calculate both TOW and Ncy in combination with climatic data.

Exploiting this new method, the urban area of Milan (Po Valley) was studied. DRH and CRH of PM samples collected within this area were experimentally measured in an Aerosol Exposure Chamber (Ferrero *et al.*, 2013, 2014). The experimental DRH and CRH values were used to accurately calculate both TOW and Ncy in Milan during the last decade (2003–2013). In this way, situ-predominant and seasonal-predominant hazards for stone substrates were identified. A comparison with the simplified methods reported in literature was also performed, and it allowed estimation of the bias that the absence of an accurate knowledge of the hysteresis loop introduce in the calculation of the hazard indicators.

MATERIALS AND METHODS

The experimental approach first required the collection of PM samples, whose DRH and CRH values were measured in a specifically-designed Aerosol Exposure Chamber (AEC). The chemical composition of PM was also analysed to interpret the seasonal variations of both DRH and CRH. Finally, meteorological data, coupled with PM DRH and CRH measures, allowed the calculation of TOW and Ncy and their seasonal behaviour over the last decade in Milan.

Sampling Activity

PM samples were collected in Milan, which represents an interesting location because it is placed in the middle of the Po Valley (North of Italy). Moreover, some important monuments are located in this area, and for these reasons

also other studies involving exposure tests for the evaluation of materials decay were performed here (Realini *et al.*, 1995; Zappia *et al.*, 1998; Kucera *et al.*, 2007). In particular, PM_{2.5} samples were collected at Torre Sarca site (45°31'19"N, 9°12'46"E) using a FAI-Hydra dual channel Low-Volume-Sampler (EN-14907, 2.3 m³/h, 24 hours of sampling time, 47 mm diameter PTFE filters Pall Corp.). A full description of the site and the related aerosol properties (chemistry, sources, vertical profiles and toxicity) is given in Ferrero *et al.* (2010, 2011b), Perrone *et al.* (2012, 2013), and Sangiorgi *et al.* (2011). Torre Sarca has been active as an atmospheric monitoring station since 2005, and its long-time series of PM_{2.5} samples collection has resulted particularly useful to estimate the TOW and Ncy over the last decade. The deposition of PM on monuments and building facades is an extremely troubled issue, in which several mechanisms may contribute (Brownian diffusion, impaction and interception due to the turbulent motions, gravitational sedimentation, thermophoresis, diffusiphoresis, electrostatic attraction) (Maro *et al.*, 2014). PM_{2.5} was chosen as it represents an important fraction in the deposition mechanism occurring on vertical surfaces (Nava *et al.*, 2010). Concerning dry deposition on vertical surfaces, the sedimentation is expected to be negligible, since it occurs mainly for the coarse fraction (i.e., PM_{2.5-10}), and the turbulent diffusion is assumed as the main mechanism (Maro *et al.*, 2014). Moreover, fine particles have a longer residence time in the atmosphere. Thus, they are able to reach higher altitudes than coarse particles even within the mixing layer itself, as PM vertical profiles in the Po Valley demonstrated (Ferrero *et al.*, 2010, 2012). Thus, PM_{2.5} particles are able to reach the whole buildings' height. Furthermore, the longer residence time of PM_{2.5} results in a smaller influence of short-range emission sources than coarse fraction. Thus, the choice of PM_{2.5} is more representative for the PM pollution overall the whole urban area of Milan.

Finally, water soluble compounds (i.e., sulphates), are generally abundant in fine PM and, because of this, PM_{2.5} is a large fraction of PM₁₀ in urban areas. In this respect, the average PM_{2.5}/PM₁₀ ratio measured at Torre Sarca during the last decade was $81 \pm 7\%$.

After collection, the PM samples were dried out and stored in darkness at -20°C at the Filter Bank of the University of Milano-Bicocca, which was specifically designed for the storage of PM samples. In order to obtain a dataset that could be representative of the Milan PM's properties during the last decade, forty PM_{2.5} samples were chosen from the Filter Bank for this study. They were uniformly distributed according to the seasons and spanning a time range from 2006 to 2013. Prior to the chemical analysis, the PM filters were cut into two halves: one half was analyzed in the AEC, while the other half was extracted to determine the chemical composition of the ionic fraction. The uniformity of PM samples on filters has been examined in a previous work (Owoade *et al.*, 2006).

Electrical Conductivity Measurements for the Determination of DRH and CRH

Aerosol deliquescence and crystallization were investigated

using an electrical conductivity method, similar to the one developed by Yang *et al.* (2006), taking advantage of the AEC: a 1 m³ environmental-controlled chamber in which it is possible to vary the relative humidity (RH) by introducing pure water vapour (humidification) or pure dry air (dehumidification). Temperature and RH in the AEC were constantly monitored by means of a DMA 572.1 thermo-hygrometric sensor connected to an ELO 008 M-LOG data-logger (LSI Lastem s.r.l.). In the AEC it is possible to achieve up to 0.5% sensitivity in terms of RH variation while temperature was set to 25°C. During both humidification and dehumidification, electrical conductivity of PM_{2.5} samples was measured in custom-built conductivity cells. These are made by two electrodes, positioned at calibrated distance, and a filter-holder. Up to six conductivity cells can be housed in the AEC, in order to perform several simultaneous conductivity measurements. Conductivity measurements were performed with an Agilent 34411A 6 ½ digital multimeter, connected to the cells by means of an Agilent L4421A 40-channels armature multiplexer. For each sample, five conductivity measurements were acquired and averaged at each RH step (step magnitude 1.0% RH). In Fig. 1, a typical conductivity curve is presented. When the particles are in a completely dry or completely wet status, the conductivity values measured during the humidification and the dehumidification steps are comparable. If the particles on the filter are dry, conductivity values are null or close to multimeter detection limit (0.0007 μS); in such a situation a little variation of RH doesn't involve significant changes in conductivity. If the particles are in a wet status, conductivity values are relatively high and the RH variation led to a quite-linear growth in terms of measured conductivity. On the other hand, during the phase transitions the two curves differ significantly, thus revealing the hysteresis loop. According to Ferrero *et al.* (2014), observing the conductivity curves registered during the humidification and dehumidification steps, it is possible to identify both a DRH and a CRH region. The DRH region occurs when a strong increase of conductivity led to the wet condition. The maximum gradient of the conductivity increase corresponds to the midpoint of the DRH region. For the purpose of this study, where it is important to identify the RH threshold above which liquid water is present, DRH_{end} point has been taken in account looking at the last measured point before the wet zone. Similarly, a CRH region is identifiable in the dehumidification curve. Consequently, the CRH_{end} point has been taken as the last measured point before the dry zone, when the conductivity comes back to the starting values. The proposed method is in agreement with Schindelholz *et al.* (2014), who performed similar measures on pure salt samples. A detailed comparison between experimental data obtained with the presented procedure and DRH and CRH values predicted by theoretical models has been reported in Ferrero *et al.* (2014).

Computing the Seasonal Profile of TOW and Ncy

As described, DRH_{end} and CRH_{end} were determined for each of the forty analyzed PM samples. DRH_{end} and CRH_{end} average values were calculated for each seasonal period: winter, summer, and spring + fall.

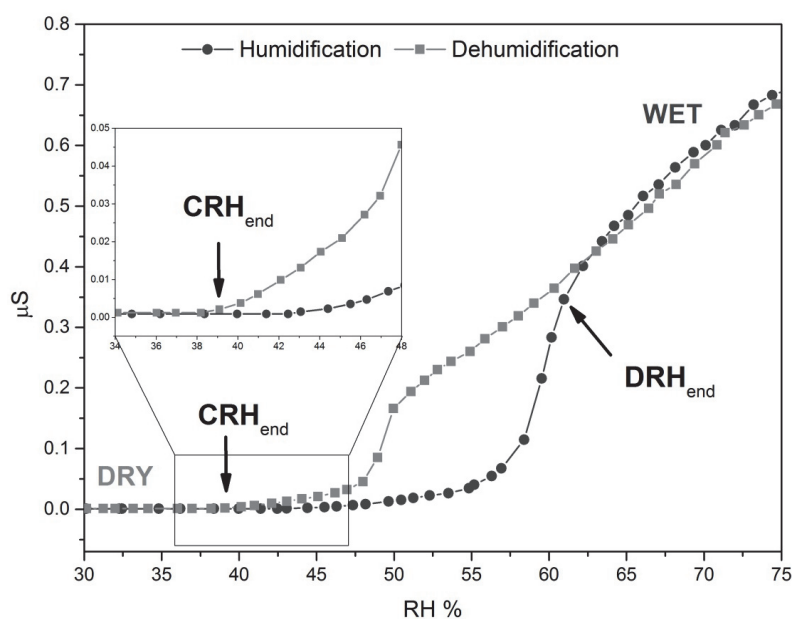


Fig. 1. Typical conductivity curve (μS) in function of humidification/dehumidification conditions ($\text{RH}\%$) obtained for a PM sample collected on a PTFE filter in Milan. DRH_{end} has been attributed looking at the humidification curve (points) when a strong increase of conductivity led to the wet condition. CRH_{end} was attributed looking at the dehumidification curve (squares) when the conductivity comes back to the starting values.

Meteorological data for the years 2003–2013 were acquired from all the meteorological stations in Milan (Lambrate 45.49N 9.26E; Brera 45.47N 9.19E; Juvara 45.47N 9.22E; Zavattari 45.47N 9.14E and Marche 45.49N 9.19E), that are controlled by the local Environmental Protection Agency (ARPA Lombardy). Hourly average values of ambient T and RH representative for the overall urban area of Milan were derived for each season.

Comparing the DRH_{end} and CRH_{end} results with ambient RH values, three different situations were identified for the state of hydration of ambient PM: 1) when $\text{RH} < \text{CRH}_{\text{end}}$, particles were “dry”; 2) when $\text{RH} > \text{DRH}_{\text{end}}$, particles were “wet”; 3) when $\text{DRH}_{\text{end}} > \text{RH} > \text{CRH}_{\text{end}}$, particles were “dry” or “wet” depending on the RH trend: if RH was decreasing from an above- DRH_{end} value, particles were still “wet” until the CRH_{end} was reached; otherwise, if RH was increasing from an under- CRH_{end} value, particles were still “dry” until DRH_{end} was reached.

From the aforementioned data and states of hydration, seasonal values of both TOW and Ncy were calculated. A cycle was counted only when RH was lower than CRH_{end} value and RH trend was decreasing from a condition in which particles were in a “wet” status (RH previously higher than DRH_{end}). TOW was determined by adding up the hours in which particles were wet: $\text{RH} > \text{DRH}_{\text{end}}$ plus the hours in which RH was decreasing from DRH_{end} to CRH_{end} . TOW was expressed as a percentage of hours in the considered period. A graphical example of the computational algorithm is shown in Fig. 2.

PM Chemical Composition

In order to discuss the seasonal variation of both DRH and CRH as a function of the seasonal PM chemistry, the

water-soluble inorganic fraction of the forty PM samples was analyzed by ion chromatography (IC) coupled to conductivity detection. First, PM samples were extracted in 3 mL of Milli-Q[®] water (18.2 M Ω) by using an ultrasonic bath (20 min, SONICA[®], SOLTEC), and the extract was filtered with a syringe filter (0.45 μm PTFE) to remove the water insoluble fraction. Cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) were analyzed using two coupled ionic chromatography systems (Dionex ICS-90 and ICS-2000). Cations were determined using a Dionex IonPac CS12A-5 analytical column: an isocratic elution was performed with 20 mM methanesulfonic acid (flow rate of 0.5 mL/min). The eluent signal was suppressed using a Dionex CMMSIII 4 mm MicroMembrane chemical suppressor. Anions were analysed using a Dionex Ion Pac AS14A-5 analytical column, a solution of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (8.0 mM/1.0 mM, Dionex056937) was employed as eluent (the flow rate was 1 mL/min). The eluent signal was suppressed by means of a Dionex AMMSIII 2 mm MicroMembrane chemical suppressor. Quantification was achieved by means of the external standard method. Standard solutions were made starting from solutions of each single ion (1000 mg/L, Fluka).

RESULTS AND DISCUSSION

DRH_{end} and CRH_{end} Values

Winter samples showed the lowest values of both DRH_{end} and CRH_{end} : $60 \pm 4\%$ and $39 \pm 6\%$, respectively. Conversely, summer samples showed the highest values of both DRH_{end} and CRH_{end} : $73 \pm 1\%$ and $52 \pm 5\%$, respectively. Fall and spring samples showed values that were very close to winter ones: DRH_{end} was $61 \pm 3\%$ while CRH_{end} was $42 \pm 4\%$. Differences between winter and summer samples and the

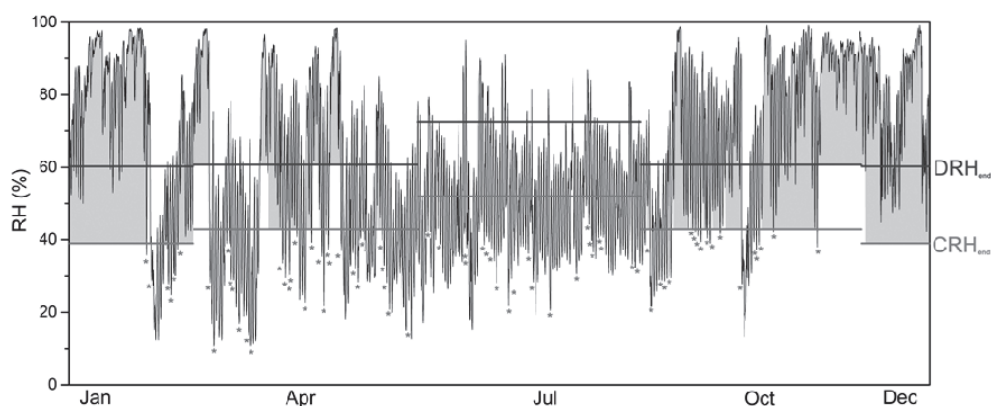


Fig. 2. Graphical representation of the algorithm used for TOW and Ncy computation for a period of one year (2009). Combining RH hourly data and seasonal average DRH_{end} and CRH_{end} , crystallization events are signed with an asterisk (and correspond to a cycle count), while in light-gray TOW is highlighted.

good agreement between winter and spring/fall samples can be explained considering the seasonally averaged chemical composition of the PM samples reported in Fig. 3. The ionic fraction accounted for $35 \pm 12\%$ of the total PM mass during all seasons, and its chemical composition changed according to the season, shifting from a nitrate-predominance ($53 \pm 12\%$ of the total inorganic ions) for the winter samples, to a sulphate-predominance ($54 \pm 17\%$ of the total inorganic ions) for the PM samples collected during summer. NH_4^+ was the main cation and its mass fraction remained quite constant both in winter and summer ($23 \pm 1\%$). The ionic fraction of spring and fall PM samples showed a chemical composition very close to winter one. The PM chemical compositional data are in agreement with the other previous studies performed in Milan (Perrone *et al.*, 2012).

The knowledge of PM's DRH_{end} and CRH_{end} could be very important to assess the potential impact of particles for heritage substrates conservation. Low DRH_{end} values suggest a high tendency of particles to adsorb water, while high CRH_{end} values suggest a tendency to crystallize even at high relative humidity. Depending on the climatic conditions, DRH_{end} and CRH_{end} values led to a high TOW or to a high frequency of crystallization events. Another relevant feature is the width of the hysteresis loop, which is computed as the difference between DRH_{end} and CRH_{end} . The average hysteresis loop was of $20 \pm 6\%$. The magnitude of the hysteresis loop can affect TOW and Ncy: for instance, for the same RH conditions, a smaller hysteresis loop led to lower TOW and higher Ncy. This is a crucial point since most of the figures reported in the literature were obtained not considering the hysteresis loop (see the introduction section) (Brimblecombe *et al.*, 2006; Bonazza *et al.*, 2009). Conversely, the experimental DRH and CRH data showed above evidenced the importance of the hysteresis loop as it will be demonstrated in the next section where the results for TOW and Ncy are presented.

Time of Wetness and Number of Dissolution/Crystallization Cycles

TOW and Ncy were computed over the period 2003–2013 in Milan. Average experimental DRH_{end} and CRH_{end}

points were assigned for every season, as previously described (DRH_{end} and CRH_{end} for spring and fall is the same).

Seasonal statistics of TOW and Ncy computed along the last decade are shown in Table 1. TOW is expressed as percentage of hours; Ncy as the absolute number of dissolution/crystallization cycles.

Winter showed a very high TOW ($89 \pm 11\%$) while Ncy reached low values (only 8% of the total number of transitions occurred in winter). Conversely, minimum values of TOW ($20 \pm 137\%$) were reached in summer when, Ncy was relatively high instead (30% of total transitions in a year occurred in summer). Regarding intermediate seasons (spring and fall), TOW showed intermediate values ($61 \pm 16\%$) in spring, while it was quite high ($83 \pm 15\%$) during fall. Ncy values were high during both these seasons since 38% and 22% of total transitions occurred in spring and fall, respectively.

In Fig. 4, monthly averaged TOW and Ncy are displayed. Coupling the two parameters in the same graph, it is possible to highlight the potential monthly-predominant kind of hazard that could affect stone surfaces. Results showed that three main situations occurred in Milan. A first situation took place in winter, when the very high TOW led to a high level of “chemical” stress, due to both the low DRH_{end} values and the high RH conditions. The low winter Ncy resulted in a low hazard of “mechanical” degradation instead. Such a situation can be considered particularly dangerous for carbonate substrates, as they are more susceptible to acid and karst attacks (Cardell-Fernández *et al.*, 2002).

A second situation took place in summer, when a “mechanical” hazard prevailed, due to the low RH conditions coupled with the high DRH_{end} values. As a result, high values of Ncy were obtained in summer, while TOW reached its annual minimum value. Such a situation can be considered more or less dangerous depending on porosity and mechanical properties of the materials, since mechanical decay-processes (such as crystallization stress) are less selective toward the stone chemical composition.

The third situation involved the intermediate seasons (spring and fall) which showed the highest level of hazard for exposed materials. In fact they were characterized by high

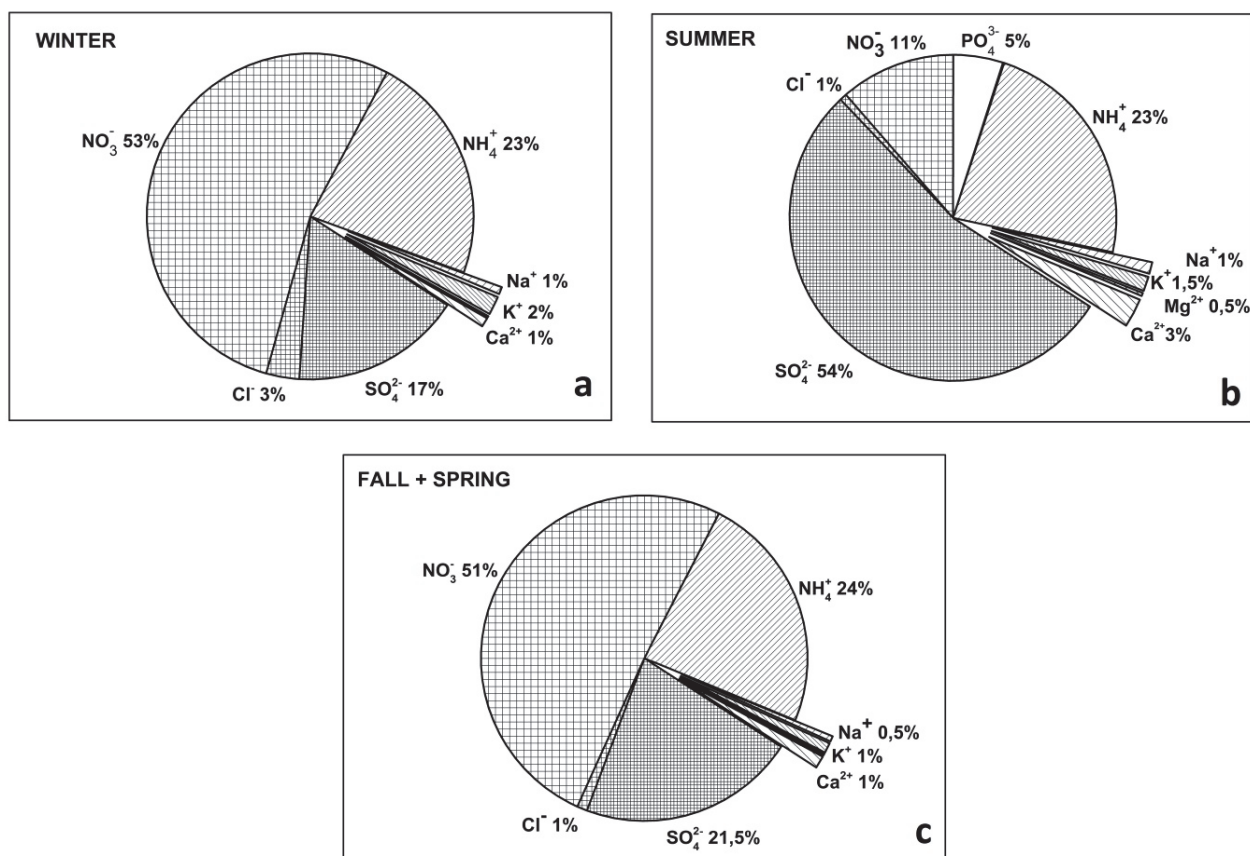


Fig. 3. Seasonal average composition of inorganic ions in PM samples collected at Torre Sarca site (Milan, Italy). Sampling period: 2006–2013.

Table 1. Seasonal statistics of N_{cv} and TOW in Milan during 2003–2013 period.

N_{cv} (\pm SD)		TOW (\pm SD)	
Total N_{cv} (2003–2013)	1221	Yearly Hours of Wetness	5518 \pm 350
Yearly Average N_{cv}	111 \pm 17	Yearly Average TOW	63% \pm 5%
Winter N_{cv} Monthly Avg	3 \pm 3	Winter TOW	89% \pm 11%
Summer N_{cv} Monthly Avg	11 \pm 5	Summer TOW	20% \pm 13%
Fall N_{cv} Monthly Avg	8 \pm 6	Fall TOW	83% \pm 15%
Spring N_{cv} Monthly Avg	14 \pm 5	Spring TOW	61% \pm 16%

values of both TOW and N_{cv} . Looking closely at the obtained results, it can be stated that in fall there was a more winter-like situation and a “chemical” hazard was prevailing while, in spring, there was a slight tendency to a summer-like situation, and a “mechanical” stress was predominant.

The aforementioned results highlighted how the proposed method considers the specific characteristics emerging by the synergy between the PM properties and the climate at the investigated site. Thus, even though the obtained results are site-specific, the method used for their determination is of general application and can be used as an efficient tool for the hazard assessment of exposed surfaces in a heritage climatology perspective.

With a similar approach the impact of climate and pollution changes in materials conservation can be evaluated. The derived information could be also useful in the decision-making process during restoration activities: for example,

if a site is subject to high percentage of TOW applying hydrophobic protective products on its exposed surfaces may be appropriate; otherwise the use of inorganic products might be more proper. Finally, the obtained results can be used to design artificial aging methods that may mimic the phase transitions and wetting behaviors of exposed surfaces with a more realistic approach.

Comparison with Other Literature Approaches

A comparison between the described computational algorithm and other literature approaches has been performed. In particular, the TOW derived in this work has been compared with the TOW calculated by assuming that the surfaces’ wetting occurs just when $RH > 80\%$ and $T > 0^\circ\text{C}$ (Brimblecombe *et al.*, 2006; Bonazza *et al.*, 2009). Results of this comparison are shown in Fig. 5(a). The two annual trends are very similar, since the wetting behavior of surfaces

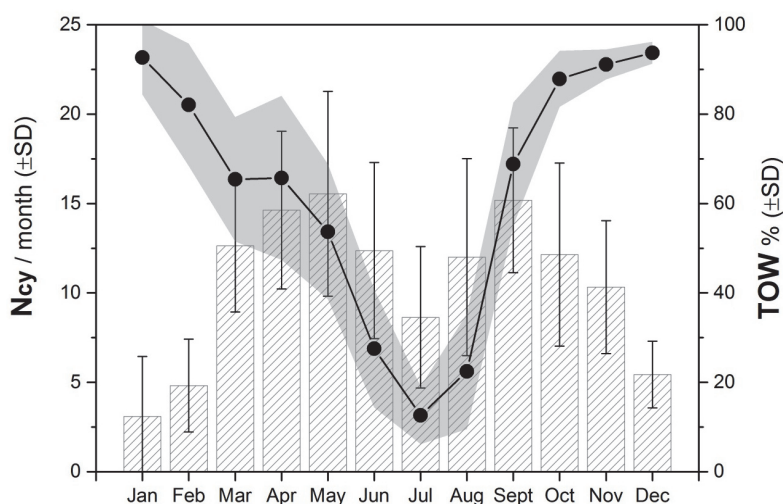


Fig. 4. Monthly averaged N_{cy} (bars) and TOW (points) in Milan during the eleven-years of study (2003–2013).

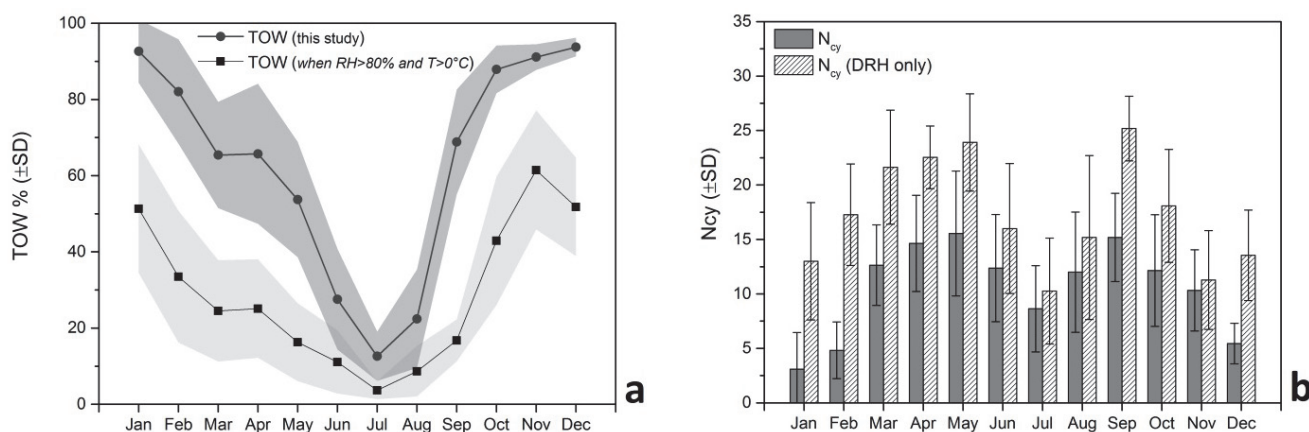


Fig. 5. Comparison between the computation methods proposed in this study and other literature approaches. a) TOW calculated using the computation routine described in this study (points) and the approach that considers time of wetness when $RH > 80\%$ and $T > 0^\circ\text{C}$ (squares). b) N_{cy} calculated considering the hysteresis loop (grey bars) and considering only the DRH (striped bars).

is strongly related to climatic conditions. However, the use of experimental values of both DRH_{end} and CRH_{end} led to higher values of TOW than those obtained by the previous literature method, especially during winter. From this comparison the role of PM and its hysteresis loop in moisture absorbing processes can be highlighted: the wetting occurring both when $RH > DRH_{end}$ (instead that $RH > 80\%$) and when $CRH_{end} < RH < DRH_{end}$ (during a dehumidification) is the reason for the differences in TOW calculated with the two methods and reported in Fig. 5(a).

A similar comparison is reported in Fig. 5(b), where the N_{cy} derived from two different computation algorithms (one considering the hysteresis and one avoiding it) is presented in order to assess the bias caused by not taking into account the hysteresis loop. The striped bars refer to the N_{cy} derived considering only the DRH_{end} (60% for winter; 73% for summer and 61% for spring and fall): in this situation crystallization events were counted each time the RH decreased under DRH. The grey bars were instead computed considering the hysteresis loop. As shown in Fig. 5(b),

without a proper knowledge of the hysteresis loop, a significant overestimation of N_{cy} can occur: about 64% more cycles/years were calculated when the hysteresis loop was neglected. The difference appeared more evident during winter.

Relationship between TOW, N_{cy} and Monthly RH Mean Values

As stated by Grossi *et al.* (2011), the study of the relationship between N_{cy} and the RH monthly mean values, could be a functional approach to extend the applicability of hazard indicators to sites where daily data are not available or to take advantage of future-climate models. At this purpose, TOW and N_{cy} calculated within this work, were related to the RH monthly average values. In Fig. 6(a), TOW values for each month of the considered 11 years are plotted against an x-variable that was calculated as the difference between the monthly averaged RH and the midpoint between DRH_{end} and CRH_{end} . This x-variable, named Transition Distance (TD), describes the “distance” of the environmental

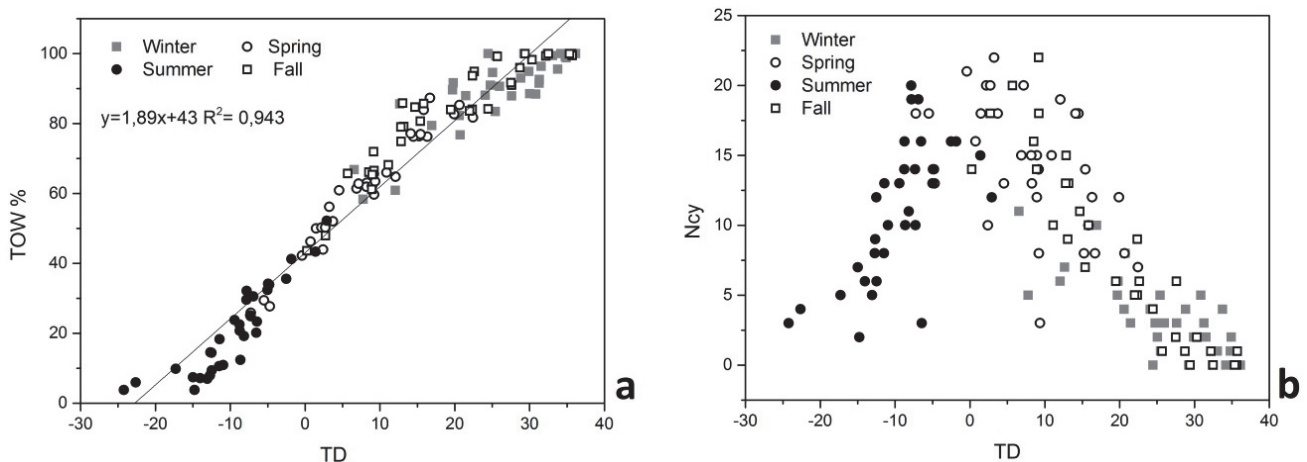


Fig. 6. a) Correlation between TOW and the “transitions distance” (TD), where TD was calculated as the difference between the monthly mean RH and the average between DRH_{end} and CRH_{end} . b) N_{cy} plotted against the same x-variable derived for the Fig. 6(a).

conditions (RH) from the aerosol properties in terms of deliquescence and crystallization (DRH_{end} – CRH_{end}). Negative values are associated to dry ambient conditions (low RH), far from promoting aerosol hydration. The opposite happens with high positive values.

A clear tendency to a linear correlation has been found between TD and TOW Fig. 6(a). Such evidence indicates that the wetting behavior of particles depends strongly on climatic conditions: the greater is the difference between the monthly RH mean value and the average between DRH_{end} and CRH_{end} , the greater is the TOW. Along with the linear trend it is possible to observe a seasonal pattern: summer months lie in the lower-part of the graph, with negative TD values and low TOW, winter points lie in the upper-part with positive TD values and high TOW. Spring points tend to arrange in the central part of the graph, while fall points are very close to winter ones.

The same correlation study was performed for the N_{cy} versus TD (Fig. 6(b)). In this case no linear trend was found. Nevertheless, some information can be derived: N_{cy} appears to be greater in the months in which the TD is close to zero while both lower and higher values of TD led to low N_{cy} . When TD is closer to 0, the monthly RH mean value lies at the midpoint between DRH_{end} and CRH_{end} ; as a result, diurnal variations of RH around the monthly mean value promote high frequency variations across DRH_{end} and CRH_{end} , resulting in a large number of N_{cy} .

In Fig. 6(b) a seasonal pattern can be identified: spring and some fall points lie in the central part of the graph while summer, winter and some fall points are spread in the side part of the graph where the TD reaches the highest values in the case of winter and the lowest in the case of summer.

The above-stated results allow a better understanding of the annual trend reported in Fig. 4. The simultaneous plot of TOW and N_{cy} shows some clear trends: both TOW and N_{cy} are decreasing shifting from May to July, while the two parameters are increasing going from July to September. Conversely, from September to April the two parameters are anti-related. This behavior is the result of the different

kind of relationship between both TOW and N_{cy} with TD.

TOW and N_{cy} Yearly Variability during the Last Decade

TOW and N_{cy} variability during the period 2003–2013 has been also analyzed. Annual values of TOW, N_{cy} , temperature and RH for the four seasons are shown in Fig. 7. Although no trends are clearly identifiable in the figures, it is possible to observe the relations between TOW, N_{cy} and the climatic characteristics of each single year, expressed through the RH and temperature seasonal average. Winter season is shown in Fig. 7(a), which shows that the years with low TOW (2003, 2005, 2006, and 2012) corresponded to years with high N_{cy} and relatively low RH. An opposite behavior was observed in years with high values of RH. Such evidence confirmed the fact that, in winter, N_{cy} and TOW were anti-related. For the summer season, Fig. 7(b) showed that years with high RH led to both high N_{cy} and TOW (2004, 2006, 2008); otherwise, years with low RH led to low N_{cy} and TOW (2003, 2005, 2009, 2012). Such evidence suggests that, contrary to winter, in summer the behavior of the two parameters (N_{cy} and TOW) shows a positive correlation.

For what concerns the spring season (Fig. 7(c)) it was possible to notice that two years with low TOW (2006, 2011) presented intermediate values of N_{cy} . Average values in terms of RH and TOW for year 2007 corresponded a high N_{cy} value. Anyway, trends in spring were less evident if compared to the results observed for winter and summer. Such tendency could be due to the wide climatic variability of the season.

Finally, during fall (Fig. 7(d)), TOW and N_{cy} showed an anti-related behavior: years with high TOW (2006, 2010, and 2012) corresponded to years with low- N_{cy} and vice-versa. From the point of view of the hazard for exposed stones, this can be considered as a further evidence of the fact that fall presents a winter-like behavior in Milan.

The aforementioned behaviors can also be better understood considering the relationship shown in Fig. 6 and the results reported in the previous section. In fact,

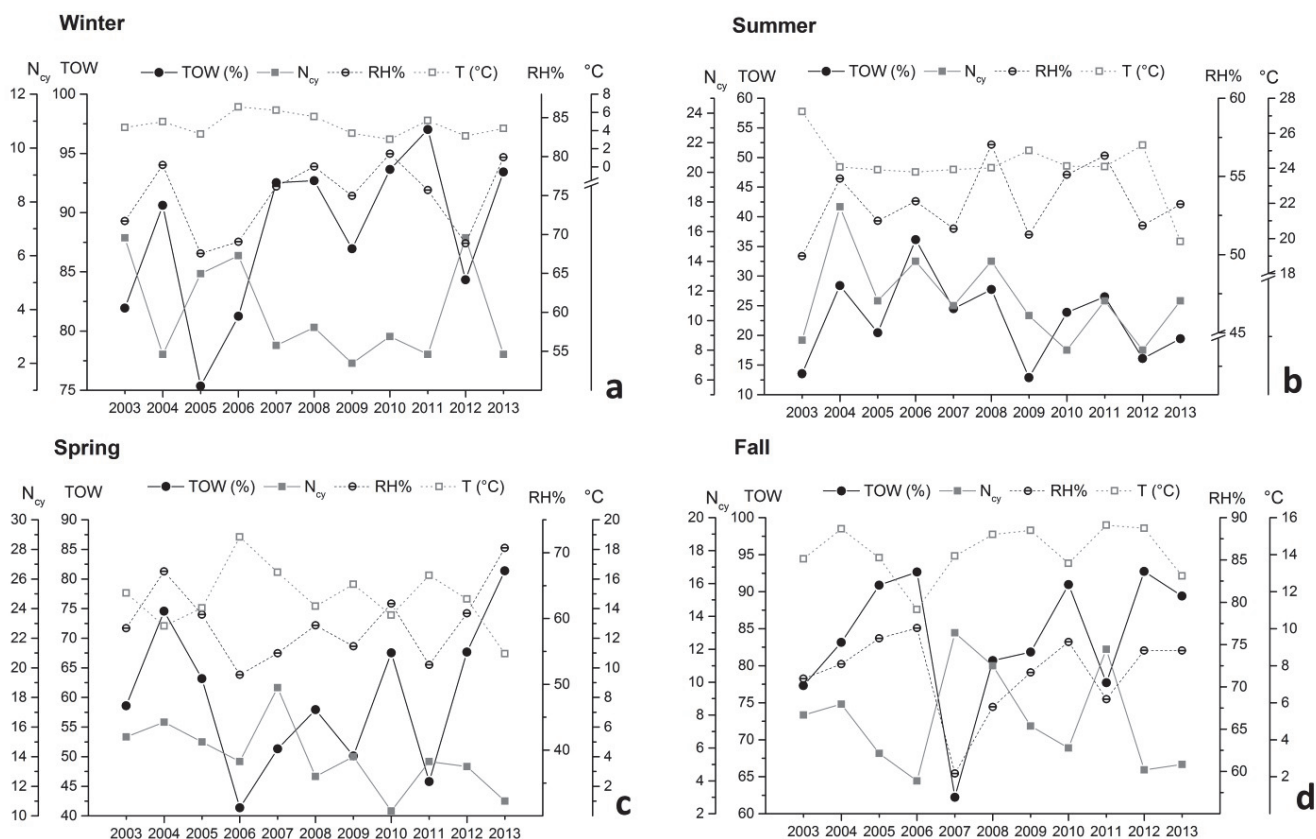


Fig. 7. Yearly variability (period 2003–2013) of seasonal values of TOW, N_{cy} , Relative Humidity (RH%) and temperature (T) in Milan.

during winter, when the TD decreases, the TOW decreases and N_{cy} increases while, in summer, an increase of the TD determines an increase of both TOW and N_{cy} .

CONCLUSIONS

In this study an innovative method was employed to evaluate the hazard for heritage stone substrates coupling experimental measurements of PM deliquescence and crystallization relative humidity with climatic data. In this respect, two hazard indicators for stone materials were determined: the time of wetness and the number of dissolution and crystallization cycles. A “chemical” hazard for stones is related to high time of wetness and a “mechanical” hazard is related to high number of cycles. The new method can be considered a new advance for the recently-introduced concept of heritage climatology.

The method was presented and applied to the case-study of Milan. Experimental measures of PM DRH_{end} and CRH_{end} in Milan showed seasonal variations that reflected the seasonal variations of PM chemical composition in Milan. DRH_{end} and CRH_{end} values were coupled with climatic data and the two hazard indicators were calculated. Observing their seasonal trend, the seasonal-predominant hazard for stone surfaces was identified for the city of Milan. In winter, a chemical hazard due to the high time of wetness and the low number of dissolution and crystallization cycles was identified. In summer, the chemical stress reached the minimum value

due to the low time of wetness while the mechanical stress increased. In spring and fall, both the time of wetness and the number of dissolution and crystallization cycles were relatively high, resulting in the greatest hazard for stone surfaces.

The differences among seasons in DRH_{end} , CRH_{end} , chemical composition, time of wetness and number of dissolution and crystallization cycles suggested that different PM chemical compositions can lead to different hazard for exposed materials.

As a conclusion, the proposed method provides a tool to make nowadays hazard-assessment which is also potentially exploitable for evaluating future situations. Even the reported results were site-specific, the method used to determine them is of general application in a heritage climatology perspective.

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