Investigation on the relationship between the environment and istria stone surfaces in Venice

Laura Falchi*

Laura.falchi@unive.it

Elisa Orio

dott.elisaorio@gmail.com

Eleonora Balliana

eleonora.balliana@unive.it~~Eleonora.balliana@unive.it~~

Francesca Caterina Izzo

fra.izzo@unive.it

Elisabetta Zendri

elizen@unive.it

Department of Environmental Sciences, Informatics, Statistics, Università Ca' Foscari di Venezia Venice Italy, Via Torino 155 Eta, 30170, Mestre, Venice, Italy

*Corresponding author. Department of Environmental Sciences, Informatics, Statistics, Università Ca' Foscari Venezia, Scientific Campus of Via Torino 155 eta, 30170, Mestre, Venice, Italy.

Abstract

Architectural limestone surfaces are particularly susceptible to decay from natural and anthropogenic acidifying gases and particulates. This investigation evaluates environmental conditions, air quality, and decay patters on Istria stone surfaces of four palaces in Venice (Italy): Ca' Bembo, Ca' Bottacin, Ca' Foscari, Ca' Dolfin. Climate parameters and air quality indicators are used to discuss the atmospheric influence on limestone and to calculate the related theoretical recession rate. Graphic assessment, surface profiling, digital microscopy, infrared spectroscopy, and x-ray fluorescence are used to assess stone surface textures and degradation patterns associated with stone decay. The morphological analysis via surface profiling using silicon mould, digitization and statistical analysis of the roughness is proposed for the assessment of stone deterioration. In particular, the methodology is used for understanding stone morphological variations in relation to parameters such as sites, exposure (sheltered or exposed area), and location (overlooking a Canal or inner court).

In relation to increasing rain amount and intensity, decreasing SO_2 and increasing NOx concentrations, theoretical limestone recession rate compatible with an urban environment (around 8 µm/year) are calculated. The morphological analysis of the sites evidences the role of the stone original texture and finish, the façade location and the specific exposure on the formation of crusts or eroded area. Buildings not recently restored (Ca' Bottacin and Ca' Bembo) present thick dendritic crusts, in particular on court side and in sheltered positions. Ca' Foscari surfaces, subjected to cleaning intervention after 2000s, show thin grey crust only in sheltered areas, reflecting the reduced presence of SO_2. Large eroded areas have been found on exposed surfaces in relation to the rain wash-out action and to high levels of NO_x.

Keywords: Istria stone surfaces; Air quality; Venice; Morphological analysis; Dendritic crusts; Architectural stone decay

1 Introduction

Air quality and climate have a severe impact on building limestone surfaces, leading to degradation phenomena such as erosion, recession, deposition, and crust formation involving substantial maintenance and protection costs (Amoroso and Fassina, 1983). For this reason, the impacts of urban environments on outdoor limestone surfaces have been deeply investigated and revised also in relation to climate changes and air composition variations occurring worldwide due to greenhouse gasses and pollutant emissions (Vidal et al., 2018; Di Turo et al., 2016; Grøntoft, 2011; Bonazza et al., 2009; Urosevic et al., 2012; Saba et al., 2018).

Nowadays, the north Adriatic coastal area demonstrates one of the highest vulnerability of limestone surfaces in relation to atmospheric changes in Italy (De Marco et al., 2017; Palagiano et al., 2018), because of the concomitant action of marine aerosol (Zendri et al., 2001a), air quality, and climate. The air quality of the area have been changing among the last century, firstly due to the industrialization between the '50es and '90es-2000 (e.g the highly pollutant district of Porto Marghera, Venice) and later to the dismantling of the plants and a new regulations for atmospheric emission in the 90es. Nowadays, $CO_{2,}$ NO_x and PMs emissions are replacing SO_x as principal pollutants in the area (Arpav and Carta, 2008; ARPAV et al., 2013; ARPAV, 2014; ARPAV, 2017; Castellari et al., 2014). According to different models, the climate of the area is expected to undergo major variations with temperature increase and drought periods followed by heavy rains (Palagiano et al., 2018; Desiato et al., 2015; Madsen et al., 2014). This changing frame requires updated evaluations of limestone surfaces degradation considering data collected over larger spans of times and in relation to future conservation policies.

The present study addresses these issues by proposing an updated analysis of the environmental impacts on Istria stone surfaces in the Venetian area, as emblematic of urban/coastal area of North Adriatic, by including a morphological characterization of Istria Stone surfaces. The study firstly reviews the environmental conditions, the air quality and the decay patterns on Istria stone surfaces observed in Venice before the 2000s, in order to identify the main degradation processes. Secondly, the air quality and climate in Venice between 2002 and 2016 period, based on available data from national and regional databases (E-ir quality, 2019; ARPAV, 2019), is presented and used to calculate the theoretical recession rate of limestone surfaces for evaluating possible modifications and hazard. For concluding, the environmental impact on the morphology of Istria stone surfaces has been evaluated analyzing four Venetian palaces, restored and not. The assessment of the surface state includes a chemical-physical characterization for individuating specific decay patterns and a statistical morphological evaluation, considering aspect such restored/non restored surfaces and the façade position (overlooking canals/courts). A novel, easy to use and economic methodology using silicone moulds was implemented for the detection and consequentially the evaluation of surface morphology and roughness.

2 Materials and methods

2.1 Literature review on the impacts on istria stone surfaces before 2000's

A literature survey was carried out regarding the main decay effects observed on Istria stone surfaces and the concomitant air quality in Venice before 2000's. Published data regarding the surfaces of ancient buildings, *ad hoc* exposed specimens, and reports regarding the main pollutants emissions were considered (Zendri et al., 2001a; ARPAV et al., 2013; Zendri et al., 2014; Zendri et al., 2001b; Zendri et al., 1994; Bertoncello et al., 1992; Maravelaki et al., 1992; Biscontin et al., 1992; Biscontin et al., 1989; Biscontin et al., 1991; Sgobbi et al., 2010; La Russa et al., 2018; Belfiore et al., 2013) and reported in the result section.

2.2 Evaluation of degradation environmental factors in 2002–2017 and estimation of limestone recession rate

For evaluating the variation of climate factors and pollutants in Venice in recent years, major climate parameters (rain amount, relative humidity Rh, temperature) and air quality indicators (SO_2, PM_{10}, $NO_{x,}$ concentrations) were selected. Their presence, concentrations and trends over the 2002–2017 period are discussed in relation to their impact on Istria stone. For this, the data of the weather stations of Istituto Cavanis in Sacca Fisola (historical city center, urban marine background) and Parco della Bissuola (Venetian mainland, urban background), collected by the Regional Agency for the Environmental Preservation and Protection of Veneto (ARPAV) and the Italian Institute for Environmental Protection and Research (ISPRA), were considered (Arpav and Carta, 2008; ARPAV et al., 2013; ARPAV, 2014; ARPAV, 2017; E-ir quality, 2019; ARPAV, 2019). Using the available ARPAV data, the dose-response function CLRTAP developed within the framework of the Multi-assess project and the Convention on Long-range Transboundary Air Pollution - was applied for calculating a theoretical limestone recession rate (R) (CLRTAP, 2014; Kucera et al., 2007; Tidbladet al., 2017):

$$R = 4 + 0.0059 \text{ x } [SO_2] \text{ x } Rh_{60} + 0.054 \text{ x Rainfall x } [H^+] + 0.078 \text{ x } [HNO_3] \text{ x } Rh_{60} + 0.0258 \text{ x} [PM_{10}]$$

Where: $[SO_2] = SO_2$ concentration (μg/m^{3}year); Rh_{60} = Relative air humidity % (Rh_{60} = Rh-60 when Rh > 60 and 0 otherwise); Rainfall = yearly amount of precipitation in mm/year; $[H^+]$ = concentration of protons in precipitation (mg/l); [PM10] = PM_{10} mean concentrations (μg/m^{3}year); $[HNO_3] = 516 \text{ x } e^{-3400/T+273)} \text{ x}([NO_2][O_3]Rh)^{0.5}$; T = temperature (°C).

This rate R may be considered as a proxy of the atmospheric hazard for limestone surfaces exposed in the Venetian context among the period 2000–2017. Due to the fact that the ARPAV data regarding $[H^+]$ in rain were not available for the whole period, a rain pH = 5 was considered for the calculation, considering the value calculated for the years 2008–2009, as reported in Grøntoft et al., 2011) (Grøntoft et al., 2011).

2.3 Evaluation of decay patterns of istria stone in four Venetian palaces

Istria stone surfaces (presumably not subjected to cleaning intervention in the last century) of three historical buildings - Ca' Bembo (CABE), Ca'Dolfin (CADOL) and Ca'Bottacin (CABOT) – were selected for evaluating the decay patterns present on Istria stone and for individuating possible different morphologies (Fig. 1). The surfaces of a fourth palace, Ca' Foscari (CF), cleaned during a conservation intervention in 2004 (Naletto et al., 2005), gave the chance to estimate some degradation processes occurred in recent years, where climate and air quality factor have been thoroughly monitored (see paragraph 2.2). The selected buildings (Fig. 1) allow a direct comparison of their decay patterns. They are, in fact, similar in terms of substrate, construction characteristics and all located within the Sestiere of Dorsoduro and are representative of ancient venetian Palaces. The buildings façades face different directions: Ca' Foscari face East the Gran Canal and West a large internal court; Ca' Bottacin and Ca' Bembo face North-East and East internal canals and west internal courts, respectively; Ca' Dolfin face an internal canal South and a

Garden on the east side. For each building, during the sampling phase two positions were taken into account: overlooking a canal and the inner court. Two exposures were also considered: sheltered areas; and areas directly exposed to rain precipitations. In the case of Ca’ Dolfin only surfaces overlooking the canal were analyzed as any Istria stone surface is present in the internal court.

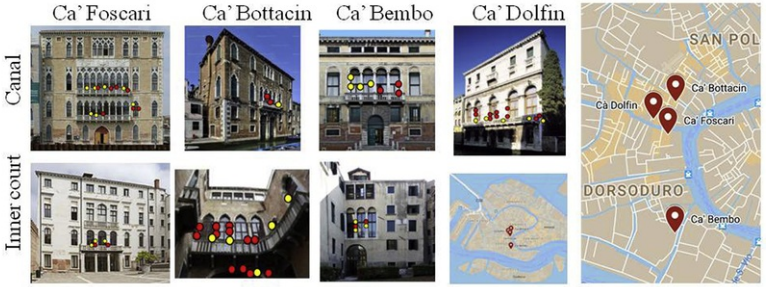

Fig. 1 Images of the case-studies façades; the red dots indicate sampling point location, the yellow dots indicate mould casting location; the maps show the buildings location within the city. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

alt-text: Fig. 1

In order to assess the presence of typical decay patterns (such as black crusts, grey patinas, eroded areas) and guide the surface profiling assessment, a non-invasive characterization of selected surfaces via photographic assessment and digital microscopy observation was integrated with Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflection mode (FTIR-ATR), and Fluorescence X-Ray analysis (XRF) on micro samples collected by scalpel. The in-situ photographic campaign and the microscopy observations were carried out with a Nikon 40D and a digital microscope Dino-Lite AM4113 at 54× and 125× magnification. The micro samples were characterized in laboratory with an Olympus SZX16 microscope; by FT-IR ATR spectroscopy with a Nicolet Nexus 670 instrument and an ATR diamond cell (64 scans with 4 cm^{-1}resolution from 4000 cm^{-1} to 400 cm^{-1} were collected for each analysis); by XRF spectroscopy with a Bruker Artax200 spectrometer (30kv, 1300 µA, 120s each scan, helium purge gas).

2.4 Surface profiling of istria stone case studies

The morphology analysis gives information on the conservation state, on the original texture of the stone (bush hammered, smooth finish), on the erosion and deposition areas, and on the possible relation with the surface location, the exposure or previous cleaning intervention (Grissom et al., 2000; López et al., 2018). A non-invasive evaluation of the surface morphology was developed using silicone moulds and profile digitization (see Fig. 2). The collected digitized profiles and the calculation of roughness parameters provides valuable data for statistical analysis and may allow future comparisons and evaluation of degradation kinetics.

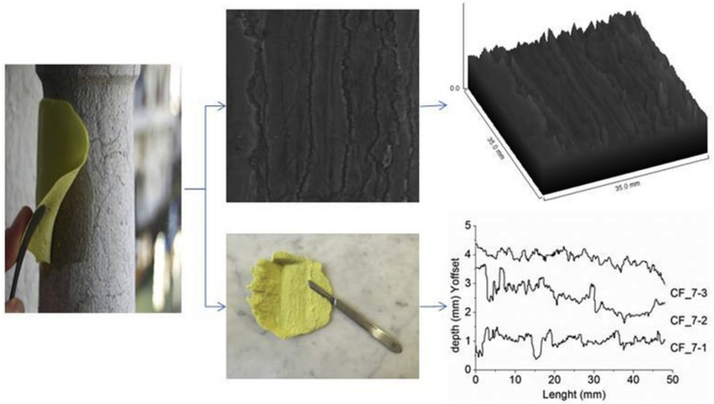

Fig. 2 Morphological evaluation of the surfaces. Left: mould detachment; above: mould scan and conversion to 3D grayscale profile; below: mould slices, side section inking, stamping and digitized 2D slices profiles.

alt-text: Fig. 2

A faithful negative reproduction of surfaces (around 5 × 5 cm) were made by applying the silicone elastomer GSP-400N® by Prochima®. After 8 h, the rubber moulds were peeled off without damage to the surfaces, thanks to the rubber high flexibility, low shrinkage, and excellent release properties; the use of release agent was not necessary.

In order to enhance the mould morphology, 600 Dpi scans of the moulds were carried out with a HP Photosmart C7280 scanner, and the FiJi® ImageJ software (Schindelin et al., 2012) was used to obtain 3D graphs based on the grey levels, following the routine: scaling, conversion in 8 bit grey image, image inversion to obtain the positive surface, and surface plot tool to obtain 3D graphs of the image's grey levels.

The surface roughness was estimated on digitized cross-profiles: the moulds were cut every 5 mm, the side sections were inked, stamped and scanned at 600 Dpi with the HP Photosmart C7280 scanner; *Web Plot Digitizer©* software (Rohatgi, 2018) was used to digitize the contours as a 2D (x-z) plot (axial resolution on z-axis of 0.01 mm). The roughness values R_a were calculated by Origin 9.1 Software for each 2D profile and used as parameter to describe the morphology (~~ISO 4287:1997, 1997~~ISO 4287:1997, 1997):

$$R_a = \frac{1}{L}\int_0^L |y|\, dx \quad \text{were y is the profile height} \tag{1}$$

In order to evaluate the reliability of the proposed methodology to existing ones, laboratory stone specimens and the corresponding moulds were measured by conoscopic laser profilometry (see Supplementary material-Evaluation of the surface profiling methodology) (Gaburro et al., 2017) The Ra results were compared obtaining a good correspondence: Ra with our methodology was 0.119 ± 0.03 mm; Ra by conoscopic laser profilometry 0.115 ± 0.01 mm (see Supplementary materials- Evaluation of the surface profiling methodology).

The statistical differences among the profiles and the data structure is evaluated applying ANOVA and regression tree models on Ra, based on three main predictor variables: palace (CF, CABOT, CADOL, CABE), position (court or canal) and exposure (exposed EX or sheltered SH).

In particular, the regression tree model is built of leaves (subset of variables values) and branches (connection of the leaves nodes), created by recursively splitting the data on the chosen predictor variables, thus individuating child nodes with smaller variability around their average than the parent node. Statistical analysis were performed by using the STATISTICA7 software (StatSoft and Inc, 2007).

3 Results and discussion

3.1 Literature review on the environmental impacts on istria stone surfaces before 2000's in Venice

In Venice, the effects of air composition on Istria stone surfaces have been deeply investigated since the 1950es (Zendri et al., 1994, 2001a, 2001b, ~~2014bib_Zendri_et_al_2001abib_Zendri_et_al_2014bib_Zendri_et_al_2014bib_Zendri_et_al_2001bbib_Zendri_et_al_1994;~~ Bertoncello et al., 1992; Maravelaki et al., 1992; Biscontin et al., 1989, 1991, 1992~~bib_Biscontin_et_al_1992bib_Biscontin_et_al_1989bib_Biscontin_et_al_1991~~; Sgobbi et al., 2010; La Russa et al., 2018; Belfiore et al., 2013). The researches pointed out how Venetian air quality has been strongly affected by the pollutants (CO_2, SOx PMx, NO_x) due to the industrial plant of Porto Marghera, the proximity to the Marco Polo airport and the maritime port, the vessel traffic, the domestic heating, the presence of marine aerosol, and the high population density of the region (Arpav and Carta, 2008; ARPAV et al., 2013). Sulphur dioxide content (Biscontin et al., 1989) was around 40–52 $\mu g/m^3$year until 1984, and decreased to 13–26 $\mu g/m^3$year from 1984 to 1988 after the introduction of a law for the conversion to methane in civil heating. NO_x level was lower than 20 $\mu g/m^3$year till the 2000's, and was not considered as a relevant decay source. PM_{10} was estimated in 1986–1987 around 60–70 $\mu g/m^3$ as average.

The cited pollutants are known to affect Istria stone surfaces and to produce three main specific decay features (Biscontin et al., 1991; La Russa et al., 2018): formation of black dendritic crusts in rain sheltered surfaces; thin black and grey crusts in half sheltered zones; white eroded surfaces in rain washing zones.

The dendritic crusts contain soluble salts due to marine aerosol and dust deposition, $PM_{x,}$ degradation products, carbon particles due to atmospheric pollution embedded in a gypsum matrix, which is formed due to acid attack of SO_x on limestone (Rodríguez-Navarro and Sebastián, 1996). The dendritic crusts are more porous than the bulk materials and undergo swelling and shrinkage due to salt dissolution and crystallization with a peel-off effect on the underlying stone. The grey crusts, present in partially exposed areas, contain in several cases calcium oxalates as well (Sgobbi et al., 2010). Recent studies (La Russa et al., 2018; Belfiore et al., 2013) essentially confirm the crust composition already observed in the past (Sgobbi et al., 2010; Rodríguez-Navarro and Sebastián, 1996): gypsum, calcite, oxalates; As, Ba due to the glass industry in Murano,; Zn, Pb linked to heavy oil combustion from ship traffic. An enrichment in Pb and Zn was found by Belfiore et al., 2013) (Belfiore et al., 2013) via LA-ICP-MS in the inner layer of one crust, attributed by the Authors to the deposition of pollutants before the ‘90es. Nevertheless, even if the influence of the location (height, exposure to sea spray deposition, distance from canals) of the crusts is already known to strongly affect the composition, it is difficult to directly correlate the crust composition found in historical buildings to the deposition period.

The washed areas, on the other side, are subjected to a constant loss of material due to run-off erosion, and few salts and gypsum are present (Bertoncello et al., 1992; Sgobbi et al., 2010; La Russa et al., 2018; Belfiore et al., 2013;

Rodríguez-Navarro and Sebastián, 1996). The outdoor recession of Istria stone was measured on specimens directly exposed to rain action in Venice during the years 1990–1991: in relation to a total rainfall of 1230 mm, a surface recession of 11.3 ± 1.2 µm was observed (Bertoncello et al., 1992).

3.2 Evaluation of selected factors impacting istria stone conservation in 2002–2017 and estimation of theoretical limestone surfaces recession by using damage function

In the 2000's the concentration trends of several atmospheric factors did change with respect to the past, consequently also their impact on Istria Stone surfaces. In order to estimate the trends of the main impact factors between 2002 and 2017, the data of ARPAV regarding the yearly mean concentrations of NO_2, SO_2, PM_{10}, O_3, the Rh%, the yearly precipitation (rain) and the resulting limestone recession have been considered and summarized in Table 1. Figs. 3 and 4 show an elaboration of the Ispra data divided by the Spring-Summer period (21st March- 23rd September) and the Fall-Winter period (24th September- 20th March) for each year.

Table 1 Summary of the ARPAV data regarding yearly mean concentration of NO_2, SO_2, PM_{10}, O_3, Rh%, Total rain precipitation, R = limestone recession calculated by using ARPAV data (ARPAV, 2019).

alt-text: Table 1

	SO_2 (µg/m³)		PM_{10} (µg/m³)		NO_2 (µg/m³)		O_3 (µg/m³)		Rain (mm/year)	Rh (%)	R (µm/year)	
	S	*B*	*S*	*B*	*S*	*B*	*S*	*B*	*C*	*C*	*S*	*B*
2002	23	7	46	46	41	29	52	56	1073	76	9,8	8,0
2003	6	5	45	48	43	41	52	56	615	70	7,0	7,1
2004	5	–	42	42	39	38	44	37	911	73	7,3	6,8
2005	10	2	40	48	35	26	60	44	763	72	7,4	6,8
2006	6	2	38	47	37	34	46	39	738	71	6,9	6,7
2007	8	2	43	47	36	34	47	39	732	70	7,0	6,6
2008	7	3	36	38	36	35	48	46	1201	75	7,8	7,4
2009	7	5	35	37	35	34	40	47	1003	76	7,6	7,6
2010	4	3	32	33	34	30	49	50	1161	77	7,1	7,4
2011	4	3	38	39	34	38	46	49	498	69	6,4	6,4
2012	3	3	34	36	32	32	42	46	555	73	6,6	6,7
2013	3	4	30	31	32	29	49	43	932	77	7,3	7,2
2014	3	3	28	28	29	27	56	48	1185	79	7,8	7,6
2015	2	2	35	35	34	28	53	41	593	74	7,0	6,6
2016	2	2	34	32	34	30	53	42	892	74	7,1	6,8
2017	2	2	36	35	35	32	59	46	601	74	7.3	7.0
Mean	**6**	**3**	**37**	**39**	**35**	**32**	**49**	**45**	**859**	**74**	**7,4**	**7,0**

R = limestone recession; S= Sacca Fisola weather station; B=Parco Bissuola weather station; C= Cavanis Institute weather station.

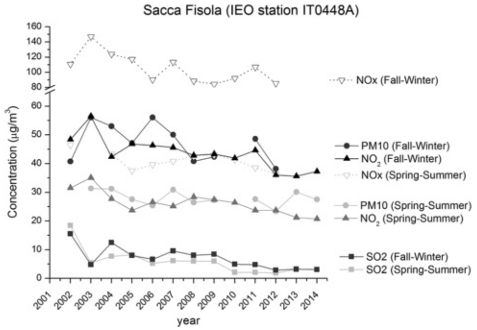

Fig. 3 Average seasonal concentration of main pollutants factor in 2002–2014 registered within the historical city center (elaboration of data from Sacca Fisola Station, the available series end in 2014 (E-ir quality, 2019; ARPAV, 2019)).

alt-text: Fig. 3

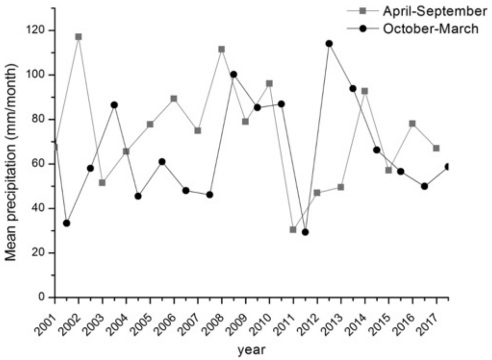

Fig. 4 Mean monthly precipitation divided by April–September and October–March periods over 2002–2017 within the historical city center (elaboration of data collected at Istituto Cavanis).

alt-text: Fig. 4

The data elaboration by seasonal division (Figs. 3 and 4) allows to observe a significant change in the average concentration of NO_x, NO_2, SO_2, PM_{10} and precipitations over the year:

- SO_2 concentration range from 20 µg/m^3 in 2002, and decrease till 2–3 µg/m^3 in the more recent years (2011–2014). From 2010 to 2011 new norms reduced the maximum sulphur content of ships and boats fuels (S max. 3.5% for BFO oils and 1% for MDO and MGO fuels) (ARPAV et al., 2013; Biscontin et al., 1991) within the Lagoon area, and the law's impact is perceptible also in the air quality data.
- NO_x data series are not complete for the considered periods, and are partially complemented by the NO_2 data. The total NO_x emissions are usually estimated to be formed by 95% NO and 5% NO_2 in relation to urban traffic (ARPAV et al., 2013). A good correlation between NO_x and NO_2 concentrations is found for spring-summer season is high ($R^2 = 0.89$), whilst the fall -winter season do not show a good correlation (regression parameter $R^2 = 0.57$) (Supplementary material-figure S-1). The main differences were measured in the fall-winter of 2005–2006 and 2006–2007, probably due to a multiplicity of sources for NO_x (e.g. industrial combustion, vehicular traffic (Arpav and Carta, 2008; ARPAV et al., 2013)). The trend for NO_2 and NO_x is only slightly decreasing in the 2002–2014 period and it is 10 times higher than SO_2 emission. The concentration in wintertime is particularly high and the mean yearly concentration is higher in comparison to the one measured at Parco della Bissuola Station, located in the Mainland (Table 1). Even higher concentration of NO_x (average of 145 µg/m^3) were measured during a short sampling (1/09/2017 till 1/08/2018) performed in Rio Novo (urban traffic weather station located nearby the considered Palaces), due to the intense marine traffic (ARPAV and Regione del Veneto, 2018). A high HNO_3 formation rate in presence of moist and rain, causing severe erosion of limestone, is expected with the measured concentrations.
- PM_{10} has a high seasonal variation in relation also to winds and to meteoric precipitations, but shows a slight decrease in the considered period. In Venice, PM_{10} is mainly composed by marine aerosol and sands with minor contribution from anthropogenic pollutants such organic carbons and metal traces, in particular As and Cd due to glass factories in Murano (ARPAV et al., 2013).

Among the considered pollutants, PM_{10} trend is inversely correlated to precipitations (Fig. 3), while NOx and SO_2 concentrations did show a slight reduction only for the rainy years 2008, 2009, 2010. Probably NOx and SO_2 are produced mainly by local sources and their concentration increase soon after each rainy event, while PM_{10} is easily washed out by the rain.

The combination of higher pollutants concentration and rainy years (e.g. in 2003) might cause severe surface wash-out and acid erosion. The calculated limestone recessions (R in Table 1) show, however, values under 8 µm/year, which is considered an acceptable threshold value for stone recession in urban environments (Vidal et al., 2018). The data differ slightly to the values obtained in De Marco et al., 2017) (De Marco et al., 2017), where a limestone recession rate over 8 µm/year were calculated. The difference in recession rate might be due to the use of different environmental data. The calculated R values show trend similar to the yearly precipitation and highlights a possible underestimation of the contribution due to acid wet deposition and marine fogs for coastal areas (Zendri et al., 2001a). Limits on the estimation of the theoretical rates were underlined also by Inkpen et al., 2012) (Inkpen et al., 2012) who found discrepancies between theoretical values and erosion of real monumental surfaces. In fact, the Recession models are usually developed considering smooth cut specimens and not historical surfaces, thus R values do not give information on heterogeneous removal of material, surface morphological and roughness variations, nature of water flow across the surfaces and memory effects, which must be experimentally assessed on exposed surfaces.

3.3 Identification of decay patterns of Istria Stone surface of four Venetian palaces

The literature survey and the discussion of ARPAV data highlighted the atmospheric variations occurred and the composition of degraded surface layers, that are linked to specific transformations of the stone morphology. These transformations can be monitored and give valuable information on the impact of the environment on the stone. In order to test this approach the selection of stone areas representative of different degradation patterns (as grey crust and washed out areas) is mandatory. Over 60 areas of Istria stone were then selected in four ancient Palaces (Ca’ Bottacin CABOT, Ca’ Bembo CABE, Ca’ Dolfin CADOL, Ca’ Foscari CF), in sheltered and exposed areas, over a canal or in internal courts.

The data collected are here summarized by showing few significant examples and discussing the main results in relation to the previous literature; Table S2 (in Supplementary materials) summarizes the results obtained divided by palace, location and exposure.

The in situ microscope observation of the surfaces (some significant examples are shown in Fig. 5) underlined the presence of black dendritic and grey crusts in the sheltered areas and white powdery surfaces on the exposed areas, as observed in previous studies (paragraph 3.1), both on façades overlooking canals or internal courts. Compared to the other buildings, the sheltered surfaces of Ca’ Foscari, restored and cleaned in 2004–2006, were brighter with lower presence of crusts.

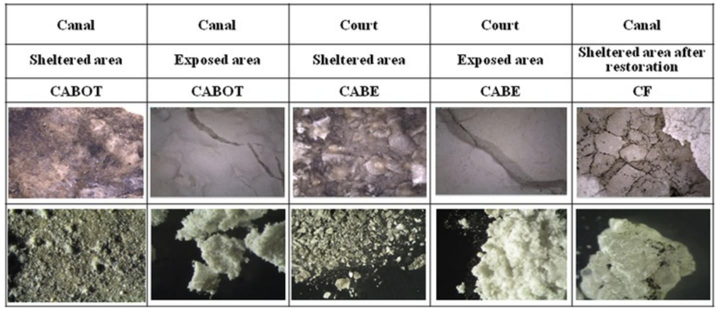

Fig. 5 Examples of different surfaces as observed by portable microscope (124X) Above, and of collected samples by optical microscope (110X) Below.

alt-text: Fig. 5

Generally, the exposed surfaces are eroded showing the sedimentation layers of the stone (Table S2). FT-IR spectra of samples collected both overlooking canals or internal courts are comparable (Fig. 6). Calcium carbonates (1400, 870, 700 $\mathrm{cm^{-1}}$) and oxalates, in form of whewellite (1650, 1315, 780 $\mathrm{cm^{-1}}$), were identified in both cases. Oxalates are possibly due to biological factors and/or degradation of organic products applied in the past. Oxalates were not detected in Ca’ Foscari, probably due to their removal during the cleaning intervention in 2004–2006 (Naletto et al., 2005).

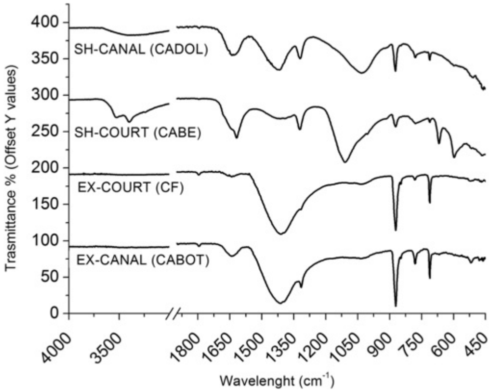

Fig. 6 FT-IR spectra significant of exposed surfaces overlooking canals -EX-CANAL (CABOT)- or overlooking the internal court –EX-COURT (CF)-, and of sheltered surfaces overlooking canals SH-CANAL(CADOL) or overlooking the internal court —SH-COURT(CABE).

alt-text: Fig. 6

The samples from sheltered areas showed different features with regards to the surface location (Table S2): tough and compact crusts adherent to the surface in areas overlooking canals; thick and non-homogeneous crusts in inner courts areas. The buildings screen the inner courts surfaces which are less subjected to wind or wind driven rain and more prone to deposition of incoherent matter, while the façades overlooking canals are more exposed to wind and draughts that carry away incoherent deposition. All the FT-IR spectra of sheltered surfaces are comparable, regardless of the provenance from façades overlooking canals or the internal courts (Fig. 6). The typical absorption bands and peaks of carbonates, sulphates (1620, 1120, 670-600 cm^{-1}), silicates (950-1100 cm^{-1}), whewellite are ascribable to the presence of calcite, gypsum due to stone acid attack, atmospheric deposition, and oxalate to biological factors or previous surface treatments, respectively. The presence of peaks ascribable to organic chains were not found in CF samples (Fig. 6), even if acrylic and siloxanes protective were applied during the 2004–2006 intervention (Naletto et al., 2005); probably those protective layer has been already removed from the rain in exposed areas or covered by deposition in sheltered areas.

The XRF analysis performed on samples from sheltered areas (Fig. 7) highlights the presence of K, Ca, Ti, Fe, Zn, Sr, Pb, S. K was detected, in particular, in surfaces overlooking the canals and can be related to the direct deposition of marine aerosol. Ca is due to the limestone and gypsum contribution, Fe may be related to the dust depositions and clay layers within Istria stone.

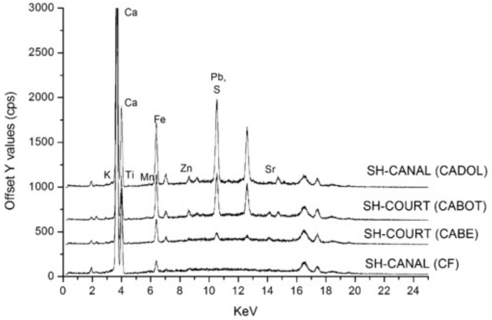

Fig. 7 XRF spectra of significant sheltered surfaces overlooking canals (SH-CANAL of Ca’ Dolfin and Ca’ Foscari) or overlooking the internal court (SH-COURT of Ca’ Bottacin and Ca’ Bembo).

alt-text: Fig. 7

The heavy metal presence (such as Pb and Sr) is most probably linked to the deposition of environmental particulate (La Russa et al., 2018). Unfortunately the peaks due to Pb and S are overlayed and their single contribution cannot be calculated; however it is possible to observe a higher peak in the internal court samples and in the canal samples of Ca’ Dolfin in comparison to Ca’ Foscari. A small amount of titanium was found in inner court surfaces.

3.4 Surface profiling

The morphological patterns were evaluated on moulds scans, 3D grey scale graphs and by analyzing the roughness factor Ra calculated from the surface profiles (Fig. 2 and attached Research Data). In relation to the reviewed literature, we choose to relate the morphological patterns observed to few significant variables: location i.e. the palace (CABE, CADOL, CABOT, CF), exposure (exposed EX or sheltered SH) and position (COURT or CANAL). Fig. 8 shows a collection of significant profiling, the relative 3D grey scale graphs, while the mean Ra grouped by palace and categorized by position and exposure are shown in Fig. 9, the raw data related to the acquisition of the profile and the statistical elaboration of the Ra measurements can be found in “research data-profilometry data. xlsx” file and in the “surface plot falchi orio. rar” divided by Palaces.

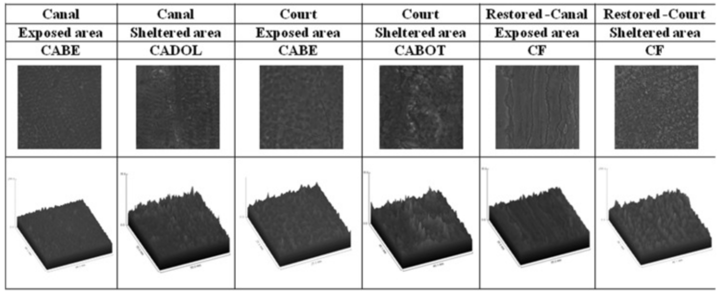

Fig. 8 Examples of scans of the silicone moulds (8-bit images, the original surfaces were 5 × 5cm wide) and 3D grey scale graphs enhancing the mould morphology. The selected images are representative of the different location end exposures and of the differences between cleane (CF) and non-cleaned surfaces.

alt-text: Fig. 8

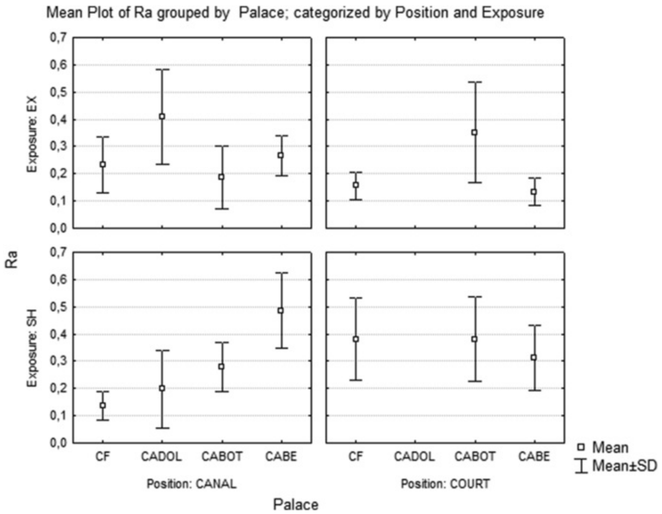

Fig. 9 Mean values of Ra grouped by palace (CF Ca’ Foscari, CADOL Ca’ Dolfin, CABOT Ca’ Bottacin, CABE Ca’ Bembo), categorized by Position (canal or court) and Exposure (SH = sheltered or EX = exposed). CADOL do not have Istria Stone surfaces located over internal court.

alt-text: Fig. 9

The observation and comparison of surface morphologies highlighted main differences in relation to the palace, rather than to the location and exposure (Fig. 8). One-way ANOVA (analysis of variance) excluding interaction factors, was performed on the Ra values grouped by palace, either by exposure, or location, in order to evaluate if there were statistically significant differences among the groups (the 4 palaces, or the 2 exposures or the 2 locations). The Ra differences between the palaces are statistically significant (F = 4,894, p = 0,003). When the Ra are considered as a whole and not belonging to a specific palace, ANOVA did not show a statistically significant difference between the data in relation to the location (F = 1.378, p = 0.241) or the exposure (F = 0.004, p = 0.983). Thus, a characteristic morphology can be identified for each palace, probably ascribable to the specific original material or finish (e. g higher/lower presence of silt veins, more or less polished or bush hammered surfaces).

To highlights differences due to the location or exposure was necessary to consider the Ra data from each palace separately. Among each palace, the comparison of mean Ra data and surface observations (Figs. 8 and 9) evidence different absolute values, but similar trends according to the position and exposure:

- Exposed areas overlooking canals show the presence of vertical ridges and grooves due to water runoff or preferential erosion along the sedimentary layers of the stone, in particular where Istria stone ashlars rich of clay veins were used (e.g. in Ca’ Foscari). The depth gauge of the grooves reaches in some cases 3 mm. The observed morphologies confirm that surfaces overlooking canals are subjected to a fast decay.
- The exposed areas overlooking internal courts are generally smoother in comparison to the canal position, showing less ridges and looked less eroded. A slight loss of the original bush-hammering finish of the stone (when present) is observed in comparison to adjacent sheltered areas.
- In sheltered areas overlooking canals, the surfaces are smoother and present lower Ra in comparison to exposed and to sheltered ones overlooking the court, with the exception of Ca’ Bembo. The presence of thin compact crusts hides the original finish and causes roughness decrease.
- Porous and thicker crusts are typical of the inner courts and cause a slight roughness increase. Some moulds collected in half exposed-half sheltered areas allow us to observe the depth gauge due to the deposits and crusts formation, particularly evident in Ca’ Dolfin and Ca’ Bottacin with steps on the z-axis exceeding 4 mm.
- Ca’ Foscari surfaces are in every location and exposure smoother in comparison to other palaces; bush-hammering finish texture is not recognizable, and grooves/ridges are present in exposed surfaces over the Canal Grande due to water runoff (depth gauge 2 mm). This smoothness may be due to a different stone original texture, to the exposure over the Canal Grande, but also to the sand-blasting cleaning done during restoration interventions (Naletto et al., 2005; Grissom et al., 2000). Newly formed thin grey crust, with a low degree of gypsum (Fig. 6), were observed over the canal and in the internal courts in sheltered areas.

A tree regression model calculated on Ra data (Fig. 10) allows to easily observe the Ra data structure and to better evaluate the influence of the selected predictor variables (location, position, exposure) and to identify possible discriminating factors. The first node divides Ca’ Foscari from the other palaces, due to the restoration intervention. Further division among the palaces can be observed at node 2, probably related to differences in the original stone texture and finish. The position (canal or court) causes divisions at nodes 3, 4, 5, then the exposure (sheltered or exposed) causes further divisions.

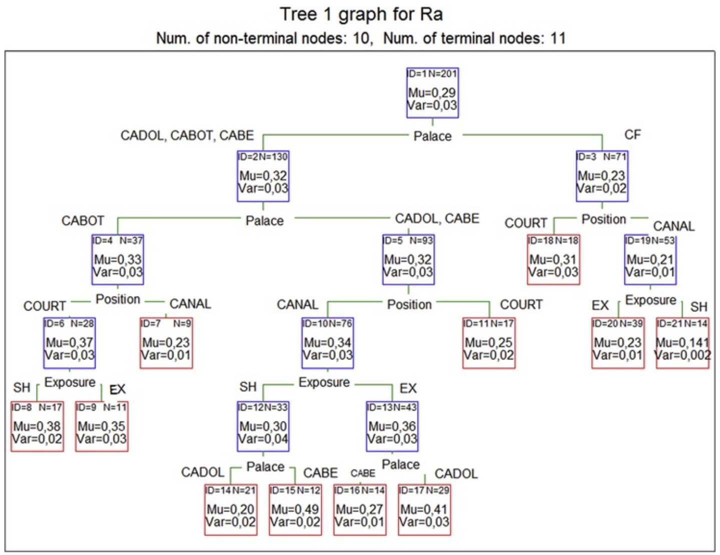

Fig. 10 Tree model graph for Ra. ID = leaf/node number, N = nr of observation in each leaf, Mu and Var = mean value and variance of Ra for each leaf.

alt-text: Fig. 10

4 Conclusions

Limestone surfaces of historical building are strongly affected by outdoor condition clearly visible by the modification of their aspect and composition. Next to the chemical-physical characterization of the decay layers present in the literature, the study of morphological variations of the surface should also be considered as meaningful for monitoring the environmental impacts. The present work focuses on proposing a methodology for characterizing stone surfaces from the morphological point of view.

The existing documentation on Venetian air quality and on architectural surface decay, implemented with the collection of new data, offered the possibility to update the relationship between the environment and the Istria stone surfaces. The collected data show that, in buildings not recently restored as in the case of Ca' Bottacin and Ca' Bembo, thick dendritic crusts are present, in particular on court side and in sheltered positions. Ca' Foscari surfaces, subjected to cleaning intervention after 2000s, showed thin grey crust only in sheltered areas, that reflect the reduced presence of SO_2 concentration. Large eroded areas have been found on exposed surfaces of the palaces, possibly due to the wash-out action of rains exacerbated by a high level of NO_x in recent years.

The application of rubber moulds and their digitalization demonstrated to be a non-expensive, reliable and affordable methodology for monitoring morphologies variation in Istria stone and for understanding the impact of the environment depending on the stone original textures, position and exposure.

The theoretical recession rate, calculated by using the air quality and precipitation data after the 2000's, is of 7–8 µm/years and, based on literature, can be considered as acceptable for urban environment. The analysis of stone morphology showed, nevertheless, eroded areas with ridges due to water runoff in every palace, with depth gauges of 2 mm also for the restored surfaces of Ca' Foscari due to the environment impact over long time span. The morphological analysis remarked that the smoothing effects together with preferential water paths are the major decay patterns on historical surfaces.

In view of this, new experimental campaigns, quantifying the material losses, become mandatory for correctly estimate the actual recession rate.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The realization of this study was possible thanks to a 1 year grant “Impact of Climate Changes on architectural surfaces in the Venetian environment” to Laura Falchi, funded by the EU JPI Project Emerisda "Effectiveness of Methods against Rising Damp in Buildings" and by the VICCS center of Ca' Foscari. We thank Prof. Claudia Daffara and Dr. Giacomo Marchioro of OpDATeCH laboratory - Università degli Studi di Verona-for assistance with conoscopic laser microprofilometry testing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.04.044.

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Appendix A. Supplementary data

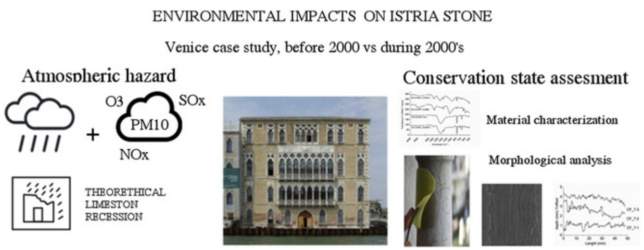
The following is the Supplementary data to this article:

Multimedia Component 1

Multimedia component 1

alt-text: Multimedia component 1

Graphical abstract



alt-text: Image 1

Highlights

- Air quality and climate impact on limestone in Venice before and after 2000.
- Evaluation of the atmospheric hazard to Istria Stone conservation during the 2000's.
- Chemical, physical, morphological assessment of Istria stone in four venetian palaces.
- Surface profiling of silicone moulds and statistical analysis of surface roughness.
- Role of surface position, location, exposure in relation to a similar environment.

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