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EFFECTS OF METEOROLOGICAL FACTORS ON THE HYDROPHOBIZATION OF SPECIFIC CALCAREOUS GEOMATERIALS FROM REPEDEA - IASI AREA, UNDER THE URBAN AMBIENTAL AIR EXPOSURE

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Abstract
Air quality in the urban environment of Iași City has declined rapidly in recent years, which requires new research focused on the effects of pollution, both on the ambiental air and on human health, as well as on apparent changes in building surfaces, including historical ones. It is common knowledge that permanent exposure to urban atmosphere triggers degradation processes on the surfaces of natural stone monuments, especially on porous stone surfaces. This research was done on samples of porous calcareous rocks similar to the natural stone used in numerous historical monuments of Iasi City. These samples were film-coated with various commercially available hydrophobization solutions. Moreover, these samples were exposed in the immediate vicinity of a road junction with intensive and growing traffic. After about seven months of exposure, the apparent changes in the treated surfaces were compared with the untreated control surfaces (control samples) subjected to the same urban air exposure conditions over the same period of time to assess the effectiveness of the coating treatment.

Keywords: *Repedea stone; Calcareous stone; Hydrophobization; Water repellent; Coating; Urban environment factors*

Introduction

It is common knowledge that there is a strong link between the local geological background and historical architectural surfaces [1, 2]. Thus, for objective reasons, mainly porous calcareous rocks from neighboring areas, such as Paun village, located on the plateau of

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Repedea Hill, were used in the Metropolitan Area of Iași City [3, 4]. Given that any natural stone is prone to a series of physical and mechanical transformations due to its exposure to environmental conditions from the moment of its extraction in the quarry or when it used in a building [5, 6], long-term research becomes necessary because these geomaterials age over time [7]. Furthermore, the strong calcareous and porous features of the Paun - Repedea stones [8-10] require the use of a coating treatment capable of preventing or limiting, as much as possible, undesirable effects [11, 12]. Also, the presence of urban air pollution factors, which has increased in recent years in the city of Iasi, has accelerated the changes occurring in building stone surface [6, 10, 13-19], which requires special attention to the use of these lithic materials in civil engineering or historic buildings.

In light of the above and at the same time knowing that there is no universal valid hydrophobic product [20, 21], this research is aimed at assessing the impact of ambient air on coated indigenous rocks, which were subsequently exposed to heavy car traffic in the urban environment for a certain period of time [22, 23]. CIE *L*a*b** colorimetry was the main research technique, useful for determining chromatic deviation on the apparent surfaces under survey [9, 24].

Experimental Part

The lithic material exposed to urban environment conditions is represented by oolitic sedimentary calcareous rock taken from Paun - Repedea village, Iasi county - Romania. Hydrophobization coating of the porous calcareous surface of the samples was carried out using eight lithic material maintenance chemicals, with the following trade names: LTP Mattstone H2O®, LTP Colour Intensifier Stainblok Seal 2®, Sikagard S700®, Sikagard S703®, Isomat Nano Pro-C®, Isomat Nano-Seal®, Isomat PS-20® and Tenax Ager®.

CIE *L*a*b** colorimetric tests were performed using a Lovibond®RT 300 (Reflectance Tintometer D65/10°) spectrophotometer used to check chromatic deviation in the same measurement spots, at each working stage. Colorimetric tests were performed in constant laboratory conditions at 21°C temperature and 60% relative humidity (RH).

After the calcareous rocks were taken from a source area located on the outskirts of Paun - Repedea village, in the southern part of Iasi City, they were cut in the form of specimens with two flat surfaces in order to make it easier to fasten them on the support and to achieve an even gravimetric deposition of particles in the atmosphere, while allowing colorimetric measurements before and after exposure in urban ambientl air. Thus, 12 samples of porous limestone were cut, dried and stored in desiccators for 48 hours, prior to the first color measurements and chemical coating treatments. Samples were marked R0.1 to R0.4 (for control samples) and R1 to R8 (for hydrophobized samples), respectively. Samples R0.1 ÷ R0.4 were used for the untreated control test, being exposed to the same urban air conditions as the eight treated samples. The hydrophobization solutions were grouped according to their manufacturers and marked S1 to S8, corresponding to the marking of the stone samples (R1 to R8) (Table 1). Hydrophobization coating was carried out in compliance with the manufacturers' technical data sheets, observing the working conditions and the quantities of solutions for each of the eight porous lithic surfaces. After this stage, the treated samples were stored and dried in laboratory conditions (for 48 hours - to stabilize surface moisture) and colorimetric measurements were subsequently performed. The data collected were labeled AT (*After chemical Treatment* - but before exposure to urban air). All porous calcareous samples (12 samples) were exposed between 8 November 2018 and 10 June 2019 (*215 days*). After the samples had been removed from the exposure area, they were dried in the same laboratory conditions for 96 hours. The last stage consisted of measuring the colorimetric deviations specific to each sample, the data collected being marked ATE (*After Treatment and Exposure*). The colorimetric data are shown in Table 2.

Table 1. Symbols used to mark hydrophobization chemicals and treated samples

Manufacturer	Chemicals		Lithic sample symbols
	Trade names	**Symbols**	
LTP	Mattstone H2O	S1	R1
	Colour Intensifier Stainblok Seal 2	S2	R2
Sika	Sikagard 700 S	S3	R3
	Sikagard 703 W	S4	R4
Isomat	Nano Pro-C	S5	R5
	Nano-Seal	S6	R6
	PS-20	S7	R7
Tenax	Ager	S8	R8

Table 2. Colorimetric ΔL^* and ΔE^*ab data collected after chemical treatment (*AT*) and after exposure to urban environment conditions (*ATE*)

Colorimetric data		R0.1	R0.2	R0.3	R0.4	R1	R2	R3	R4	R5	R6	R7	R8
ΔL^*	AT	0	0	0	0	-2.7	-1.87	-3.62	-1.57	-1.98	-3.99	-2.19	-10.45
	ATE	-1.81	-2.24	-3.37	-2.52	-6.59	-6.32	-7.88	-8.99	-5.19	-9.88	-4.94	-13.52
ΔE^*_{ab}	AT	0	0	0	0	3.67	4.35	6.34	3.49	2.54	5.51	3.81	12.16
	ATE	1.88	2.52	3.95	2.54	6.64	6.34	8.06	9.21	5.35	10.09	5.26	13.96

As concerns colorimetric evolution, color changes were measured for each coordinate (L^*, a^*, b^*) and compared to the initial values, on the same sample and in the same spot, while chromatic deviation (ΔE^*_{ab}) was calculated according to the following equation [9, 24-33]:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where:

- L^* is the change of brightness in that spot, before and after the application of hydrophobizing solutions, or before and after exposure to certain conditions, at different time intervals (n), compared to the initial (i) value: $\Delta L^* = L^*_n - L^*_i$;
- a^* is the color change of the coordinates on the a^* axis (from red to green), in the same spot, at different time intervals, compared to the initial value: $\Delta a^* = a^*_n - a^*_i$;
- b^* is the color change of the coordinates on the b^* axis (from yellow to blue), by applying the same calculation method: $\Delta b^* = b^*_n - b^*_i$ (Fig. 1).

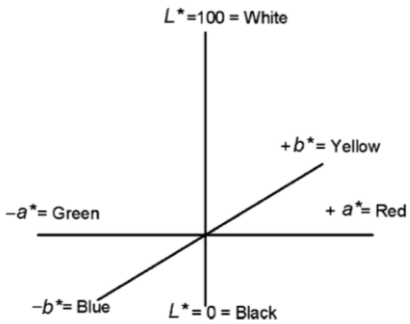

Fig. 1. Schematic representation of colorimetric coordinates L^*, a^*, b^* [27]

The urban exposure area is in the immediate vicinity of the road junction called *Podul Ros*, which is a very busy area, with intesive and increasing car traffic, having the following geographical coordinates: 47.1521932 N, 27.5869153,17 E (Fig. 2).

Fig. 2. Exposure area of the 12 samples (R building – Faculty of Civil Engineering and Building Services), closer to *Podul Ros* (*Red Bridge*) road junction

Results and Discussions

Coating Assessment by Colorimetric Measurements

As one may easily notice in Table 2 and in the chart of Figure 3, after the chemical treatment, the overall color value (ΔE^*_{ab}) ranges between 2.54 (sample R5, with solution S5) and 12.16 (sample R8/solution S8).

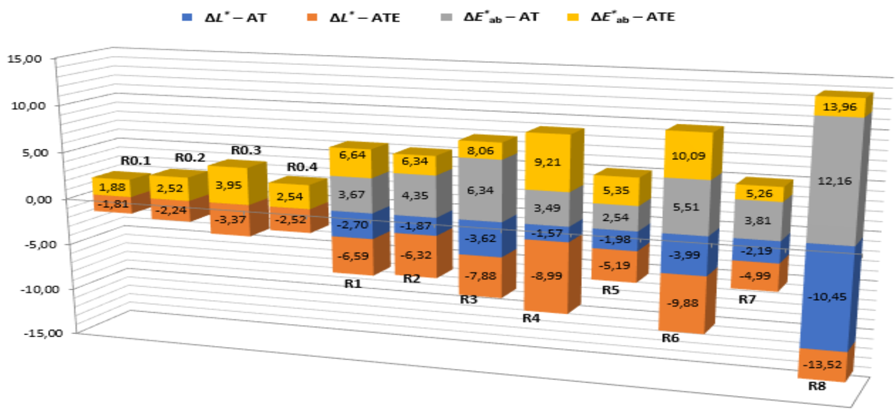

Fig. 3. Comparative graphical representation of colorimetric data Δ*E**ab and Δ*L** collected after chemical treatment (*AT*) and after exposure (*ATE*) in urban air conditions, in the *Podul Ros – Iasi* area

However, samples R3 and R6 have values slightly above the minimum ΔE^*_{ab} value, in line with literature data, which only consider notable values equal to or greater than 5 units [27]. Thus, ΔE^*_{ab} = 6.34 in R3 and ΔE^*_{ab} = 5.51 in R6. The color deviation value in sample R8 confirms the manufacturer's specifications for solution S8, in terms of obtaining the apparently *'wet'* effect on the treated lithic surfaces, which is very important to note, as it will greatly influence the aesthetics of any architectural surface (including historical ones), treated with this chemical product. For samples R1, R2, R4, R5 and P7, after chemical treatment (AT), the overall chromatic deviation values were below the mentioned limit: $\Delta E^*_{ab} \leq 5$ [27].

Coating Assessment by Colorimetric Measurements after Exposure to Urban Ambiental Air

After exposure to the urban climate in the *Podul Ros (Red Bridge) – Iasi City* area, all eight chemically treated samples exceeded the minimum threshold for significant change in color deviation ($\Delta E^*_{ab} \geq 5$), with remarkable values for samples R4, R6 and R8, ΔE^*_{ab} - ATE having 9.21, 10.09 and 13.96 units, respectively. Nevertheless, none of the control samples (R0.1 ÷ R0.4) showed significant color changes, with values ranging between 1.88 for R0.1 and 3.95 for R0.3. On the other hand, after exposure in the urban environment, all eight chemically coated samples had a tendency to change their apparent color from grayish yellow (or yellowish gray) to gray (Fig. 4.). This is accounted for by the:

- ✓ high porosity of the samples [8], which may make them more prone to retaining airborne particles from the atmosphere on their lithic surface [34];
- ✓ corroboration of wet and dry deposition procedures, depending on different weather conditions, at different times of the year [5; 35-36].

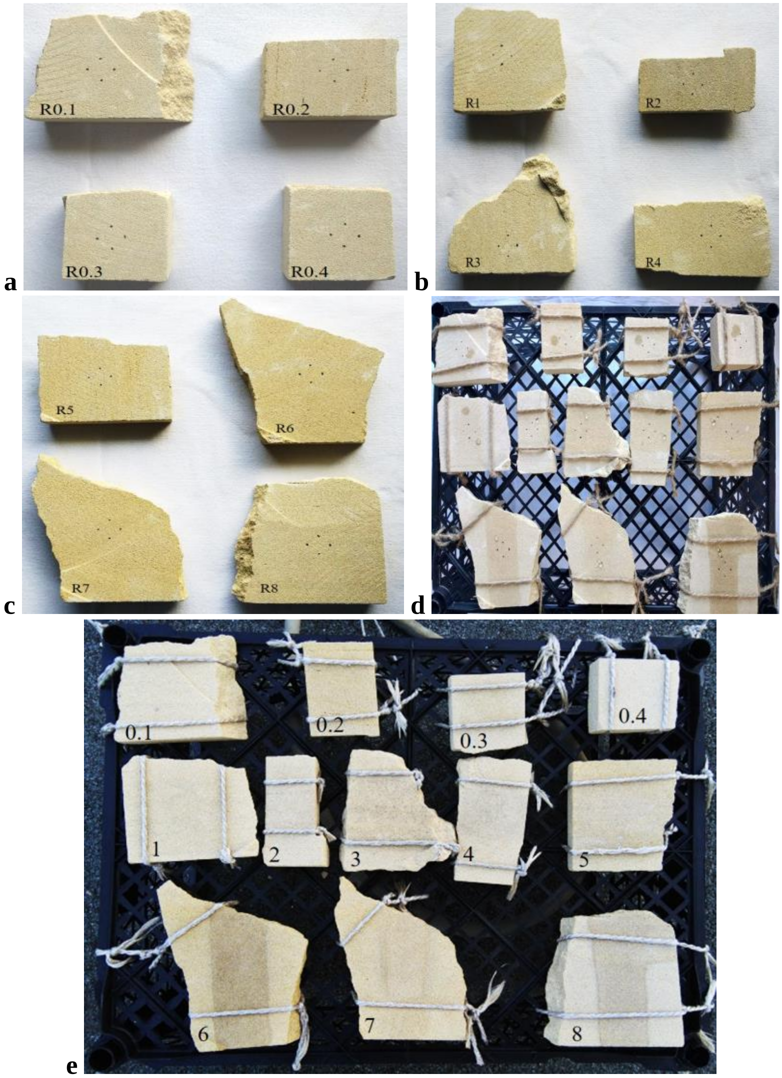

Fig. 4. Calcareous rock samples taken from the Repedea – Iasi area: **a**, **b**, **c** – before the chemical hydrophobization treatment; **d** – photograph taken before their exposure to urban environment (AT); **e** – photograph taken after 215 days of exposure in the *Podu Ros – Iasi* road junction area (ATE).

As shown by the data in Table 2 and the graphical representation in Figure 3, all ΔL^* - ATE luminescence values are substantially equal to ΔE^*_{ab} - ATE, which means that other colorimetric parameters involved in chromatic deviation (Δa^* - ATE and Δb^* - ATE) have an insignificant (or very low) influence. In literature, this phenomenon is explained by *the blackening process*, which is assimilated to major fluctuations in luminescence, ΔL^* having only negative values, by decreasing the corresponding L^* values, compared to the initial value [36].

This is true for all samples exposed in urban areas, in the *Podul Ros - Iasi City* area for 215 days, which may preliminarily confirm that local porous geomaterials are more prone to retaining suspended atmospheric particles, even when they were chemically treated to protect them from the unwanted effects of moisture. In fact, it should be noted that ultimately the main role of these coatings is the periodic maintenance of the apparent architectural surfaces [22].

A good example to illustrate this assumption is that the chromatic variation from its initial condition, after the chemical treatment of sample R4, is rather small (ΔE^*_{ab} - AT = 3.49) and, after exposure in urban areas, ΔE^*_{ab} increases significantly, reaching the limit of 9.21, i.e. more than four units compared to the minimum ΔE^*_{ab} = 5 threshold [27]. It is noted instead that the results of **sample R8** show ***lower*** *receptivity* (or *susceptibility*) to retain suspended atmospheric particles, as (after chemical treatment using S8) ΔE^*_{ab} - AT is 12.16 units (being the peak value in the ΔE^*_{ab} – AT series) and, after exposure in urban areas, ΔE^*_{ab} - ATE is very close to ΔE^*_{ab} – AT (13.96 units - which is also the peak ΔE^*_{ab} - ATE value in that series). This particular receptivity of hydrophobized porous lithic surfaces should of course be further analyzed and studied in a more extensive manner in order to draw a generally valid conclusion for treatments with solution S8 or other similar commercial products.

Influence of Urban Ambient Air Conditions on the Porous Film-coated Surfaces

As is well known, various environmental factors influence apparent architectural surfaces the most [5-6; 35-36]. Therefore, the meteorological parameters measured during the exposure of the 12 samples in the *Podul Ros* area were: *temperature*, *rainfall*, *atmospheric pressure*, *snow depth*, *wind* and *nebulosity* (cloud cover), according to the data in figures 5, 6, 7, 8 and 9.

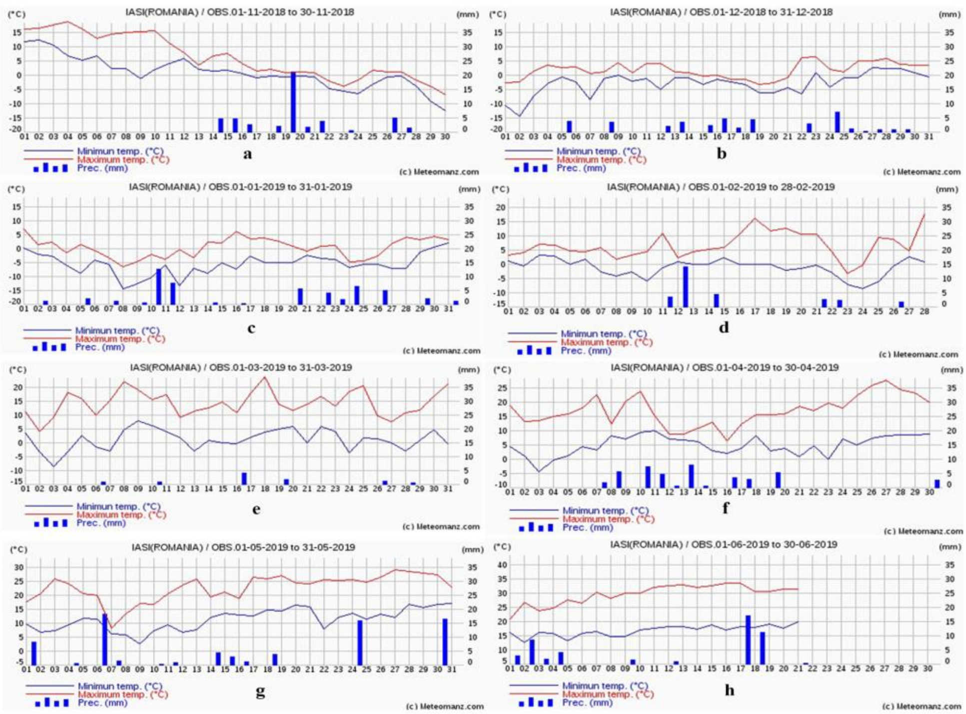

Fig. 5. Temperatures and rainfall: **a**. Nov. 2018; **b**. Dec. 2018; **c**. Jan.2019; **d**. Feb. 2019; **e**. March 2019; **f**. Apr. 2019; **g**. May 2019; **h**. June 2019

According to the presented figures, following the monitoring of the weather parameters during the exposure period of the 12 samples, the following conclusions may be drawn:

- ✓ there were 72 days of snow in total during the exposure period, which had a direct influence on the deposition of pollutants and suspended particles on the analyzed lithic surfaces [37, 38];
- ✓ there were 34 days of heavy rainfall during the spring months (March – May 2019), which had the same influence on the analyzed specimens [37];
- ✓ as far as *nebulosity* is concerned, a cloud cover of 100% (8 eighths out of 8) was noted in 50% of cases (both during the day and at night), which meant that the dispersion of pollutants was very low, thus increasing the risk of their deposition on the soil and on the anayzed lithic surfaces [39];
- ✓ the variation range of the ambient temperature was up to 45°C (i.e. between -15°C and 30°C), which meant an additional stress factor on the analyzed samples;
- ✓ wind direction was predominantly W, WNW, NW, ESE and E, with predominant speeds of 6 ÷ 8 m/s, which influences over time the occurrence of lithic material alterations predominantly on these directions.

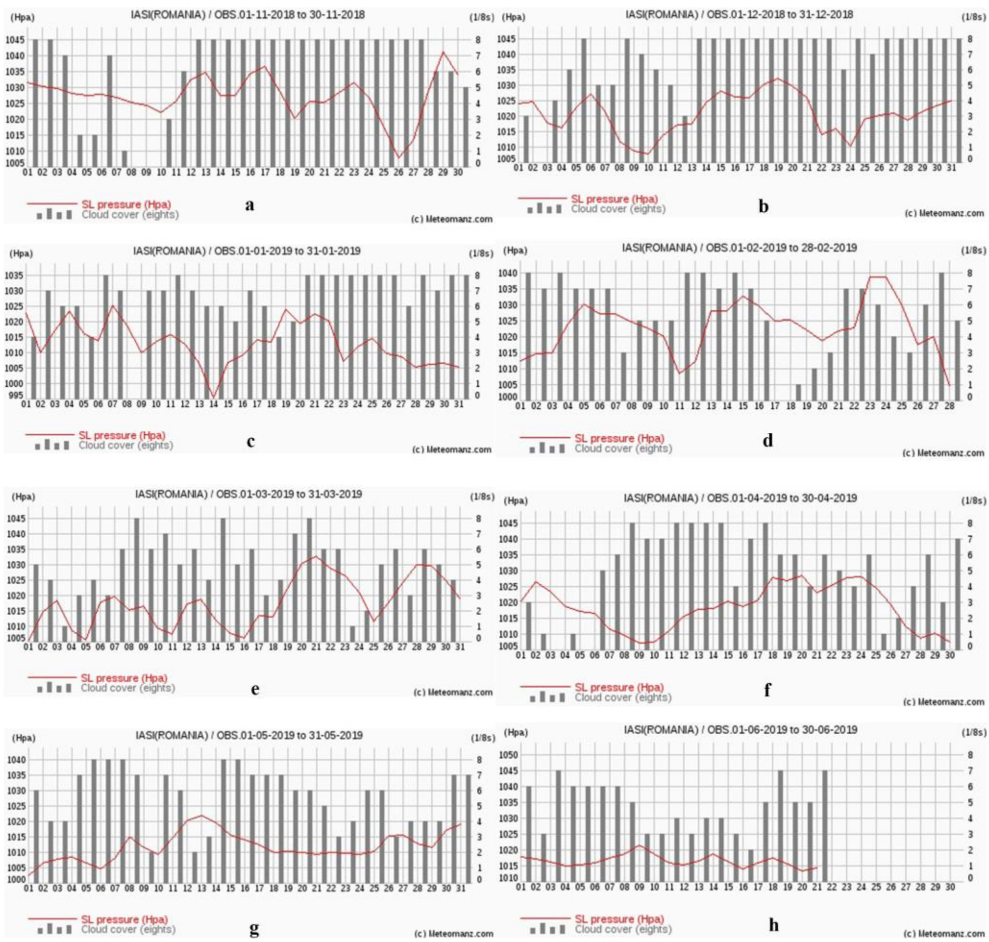

Fig. 6. Variation in atmospheric pressure and nebulosity: **a**. Nov. 2018; **b**. Dec. 2018; **c**. Jan.2019; **d**. Feb. 2019; **e**. March 2019; **f**. Apr. 2019; **g**. May 2019; **h**. June 2019

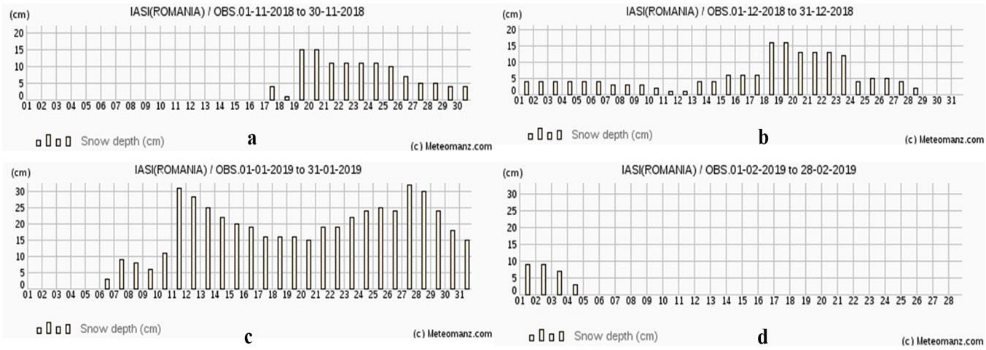

Fig. 7. Variation in snow depth in: **a**. Nov. 2018; **b**. Dec. 2018; **c**. Jan.2019; **d**. Feb. 2019

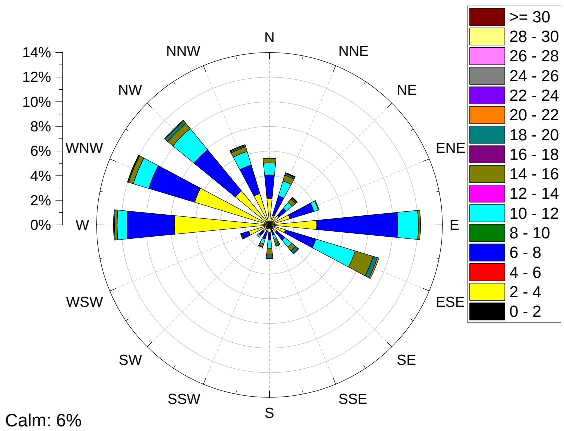

Fig. 8. Wind rose during the 215 days of urban exposure (ATE)

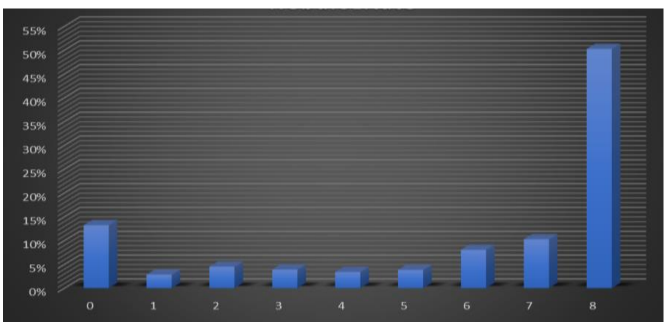

Fig. 9. Nebulosity during the 215 days of exposure (ATE)

Considering the above, the main factor that caused the color of the analyzed lithic surfaces to change was also due to the level of pollution in the urban ambient air [19]. Due to the specificity of the *Podul Ros* road junction area in the exposure period, the weather conditions help pollutants to remain on the ground level. Due to the amounts of precipitation (heavy snow and rainfall), a correlation between the pollution level and color change is also very likely. Moreover, the *'aging'* of the analyzed samples may also be blamed on the presence of pollutants on these surfaces, which contributed to the apparent color changes. The visible increase in car traffic confirms the opinion of many authors on the combined influence of these parameters on the progressive change and modification of urban ambient air, ultimately favoring the undesirable *blackening effect* revealed by our research [35-41]

These factors, the geomorphology of the Metropolitan Area of Iasi City and the local climate factors generate the thermal inversion effects specific to the cold season [42], which prevents atmospheric pollutants from dispersing and which *'pushes'* them to the ground. Over time, this influences the quality of the apparent lithic surfaces of the built environment, an assumption which is also supported by the apparent dark color (from yellow-gray to black-gray) of the 12 analyzed samples, after exposure of about 215 days in the low altitude area in *Podul Ros (Red Bridge)*, in comparison with the hilly surroundings of Iasi City - Romania.

Conclusions

The following features may be assessed based on the CIE *L*a*b** colorimetric measurements conducted on the 12 samples of porous calcareous sedimentary rock:

- ✓ the evolution of the color before and after the chemical treatments allows a first evaluation of the aesthetic impact for the research or maintenance of the apparent surfaces;
- ✓ the predisposition (or *receptivity*) of porous surfaces (including hydrophobic ones) for retaining atmospheric particles or pollutants;
- ✓ the direct influence of certain urban climate parameters on the unwanted changes occurring in porous lithic surfaces, resulting in undesirable effects such as *blackening* and future development of *black crusts*.

The response of some local lithic materials to retain atmospheric particles, together with the blackened appearance of the samples after about seven months of exposure near an important road junction in the city of Iasi (*Podul Ros* roundabout) also confirms that a number of geomaterials on architectural surfaces (including on the surfaces of historical buildings) become witnesses to the way air pollution unfolds over time, especially in urban areas.

These findings are of course only a *preliminary assessment* of the impact and of the link between:

- ✓ the porosity of some surfaces of indigenous lithic materials;
- ✓ hydrophobized surfaces and
- ✓ various environmental and meteorological factors.

Last but not least, it is worth mentioning that, for a complete technical assessment, the contact angle after chemical treatments and after exposure of porous lithic samples to different urban ambient air conditions, affected by anthropogenic crowds and intensive car traffic, needs to be successively measured. As far as the performance of the coating product involved in the process is concerned, their main purpose (hydrophobization, including in the heavily anthropized urban environment) is confirmed. It is recommended that only products that do not change the aesthetics and appearance of the buildings be used. The use of commercial products that are prone to *additionally retain pollutants* and *particles suspended in the ambient air, especially in the current very crowded urban environment*, should also be avoided.

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