"AUREL VLAICU" UNIVERSITY OF ARAD
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FIELD: ENVIRONMENTAL ENGINEERING

ABSTRACT

RESEARCH ON MEDIEVAL HERITAGE CONSERVATION IN SUSTAINABLE URBAN DEVELOPMENT

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INTRODUCTION

The United Nations Stockholm Conference in 1972 highlighted that the economic development model based on continued growth in consumption and overdevelopment in many developing countries cannot be a sustainable process and may have irreversible effects on ecosystems and heritage [1]. These ideal policies should not only aim at preserving the past, but also at securing resources for the future.

The literature deals closely with the concept of heritage and sustainability, exploring the different consequences or benefits of different principles and approaches applied in heritage conservation policies and procedures as well as in sustainable development projects. Both concepts are elements within the value system that define them and give them a specific status in the social context. Therefore, heritage conservation and sustainability concerns are closely influenced by policy actions, which may value one heritage monument more or less than another.

A widely discussed example is the case of Place Royale in downtown Quebec City, Canada. This part of the city has enjoyed extensive urban renewal and emergence from anonymity due to nationalist motivations at the end of the 20th century [2]. Such examples can easily be found in the history of each country, which shows that concepts of heritage and sustainability are mainly influenced by social and historical phenomena of ideological contexts. Heritage restoration and conservation processes as well as the development of intervention programmes that focus on sustainability involve day-to-day decisions about the interpretation, access and use of these elements [3]. This process requires increased financial and human resources, which are often difficult to obtain and implement correctly. At the same time, even if a heritage site, for example, is a unique element in the context of World Heritage, conservation and restoration decisions will be anchored in an overall strategy that reflects the concerns of the communities concerned when considering interventions in their heritage [3].

Air pollution continues to be a major challenge for modern cities. This problem not only requires the development and implementation of effective legislation to control and optimise traffic in congested urban areas, but also highlights the urgent need to protect cultural heritage. Its preservation is often neglected in the fight against the harmful effects of pollution, which can damage valuable historical structures and other important elements of cultural heritage. In recent years, poor construction management planning in affected urban areas has induced significant changes in people's living standards and quality of life [4].

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The natural conditions imposed by climate/climate change in certain regions have caused numerous visible and harmful consequences (demolition of buildings, landslides, acute need to improve the management of different soil types, etc.) [5, 6]. Moreover, traffic emissions are considered as a source of harmful pollution, resulting in particulate matter (PM), SO_2, nitrogen dioxide (NO_2), etc., all of which contribute significantly to the deterioration of building materials, especially in the case of structures considered part of a country's cultural heritage [7].

The development of heating systems for homes, buildings and industries that are no longer mainly dependent on the well-known fossil fuels has seen significant progress in reducing emissions of pollutants such as sulphur dioxide (SO_2) over the last few decades [8, 9].

OBJECTIVE

This work aims to analyse and assess the impact of air pollution on medieval heritage buildings in Brașov, with a particular focus on historical monuments. The work aims to determine the composition of the air around these monuments, identify the sources and levels of pollutants and investigate the effects of these pollutants on building materials, particularly brick and mortar. By using advanced analytical methods such as Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR), scanning electron microscopy with energy dispersive X-ray (SEM-EDX) and X-ray diffraction (XRD) and gas chromatography coupled to mass spectrometry (GC-MS), the study aims to provide a detailed understanding of the degradation processes caused by air pollution and to contribute to the development of effective strategies for the conservation and protection of Brașov's cultural heritage.

The paper has the following objectives:

1. **To determine the air composition in the vicinity of historical monuments in Brașov:**
   - To carry out measurements to identify the concentrations of volatile organic pollutants (benzene, toluene, xylenes, terpenes) around the monuments of the Black Church and the Black Tower.
   - Monitoring concentrations of air pollutants (PM_{10}, NO_2, SO_2, carbon oxides) over an extended period, using data from monitoring stations in Brașov.
2. **Analysis of the impact of pollution on construction materials:**
   - FTIR-ATR investigation of brick and mortar samples taken from inside and outside areas of heritage buildings.
   - Identification of degradation compounds and secondary forming minerals, such as calcite, oxalates and sulphates, in building materials.
3. **Assessment of microstructural and chemical changes:**
   - Using SEM-EDX analysis to examine the morphology and elemental composition of weathering crusts and biocrusts formed on the surface of bricks and mortar.
   - Determine microstructural changes due to the formation of ettringite and other hydration by-products.
4. **Determination of the organic composition of deposits:**
   - Analysis of organic deposits by gas chromatography coupled with mass spectrometry to identify organic substances accumulated on surfaces exposed to pollution.

EXPERIMENTAL PART
CHAPTER 3. THE MEDIEVAL BUILDINGS OF BRAȘOV

Brașov is located in the centre of Romania, 161 km from the capital Bucharest. The medieval town is situated at an average altitude of 625 m, in the inner curve of the Carpathians, bordered to the south and south-east by the Postăvaru Massif, which is penetrated by a spur (Tâmpa) into the town, and by Piatra Mare. The municipality covers an area of 267.32 km².

Figure 1. Satellite photos of Romania and Brașov city centre www.googlemap.ro (accessed 23.12.2023)

Gradually, in the process of development, Brașov incorporated into its structure the villages Noua, Dârste, Honterus (today Astra district) and Stupini. By incorporating the Postăvaru peak into its structure, Brașov is the city at the highest altitude in Romania. The inhabited medieval fortress of Brașov is one of the most crowded fortresses in Europe, preserving historical and cultural relics of unique architecture. Medieval Brașov is known for its uniqueness, thanks to the preservation and restoration of the buildings preserved on the old sites.

The Citadel of Brașov has sights of great tourist attraction: the Black Church, the Council House, the Ecaterina Gate, the Cojocarilor Bastion, the Postăvarilor Bastion, the Weavers Bastion, the Blacksmiths Bastion, the Grănicerilor Bastion, the Graft Bastion, the White Tower, the Black Tower, the Butchers Tower, the First Romanian School in the courtyard of the church of Saint Nicholas. All these medieval historical and cultural sites have a sustainable development that meets the needs of the present generations without harming the interests of future generations. In the following, the seven monuments subject to research in this paper are presented.

CHAPTER 4. MATERIALS AND METHODS

4.1. Sampling

Brick samples were taken from seven historic buildings in Braşov in Transylvania, Romania (presented in Chapter 3) except for the White Tower. The locations of these heritage buildings in the city of Braşov are illustrated in Figure 2.

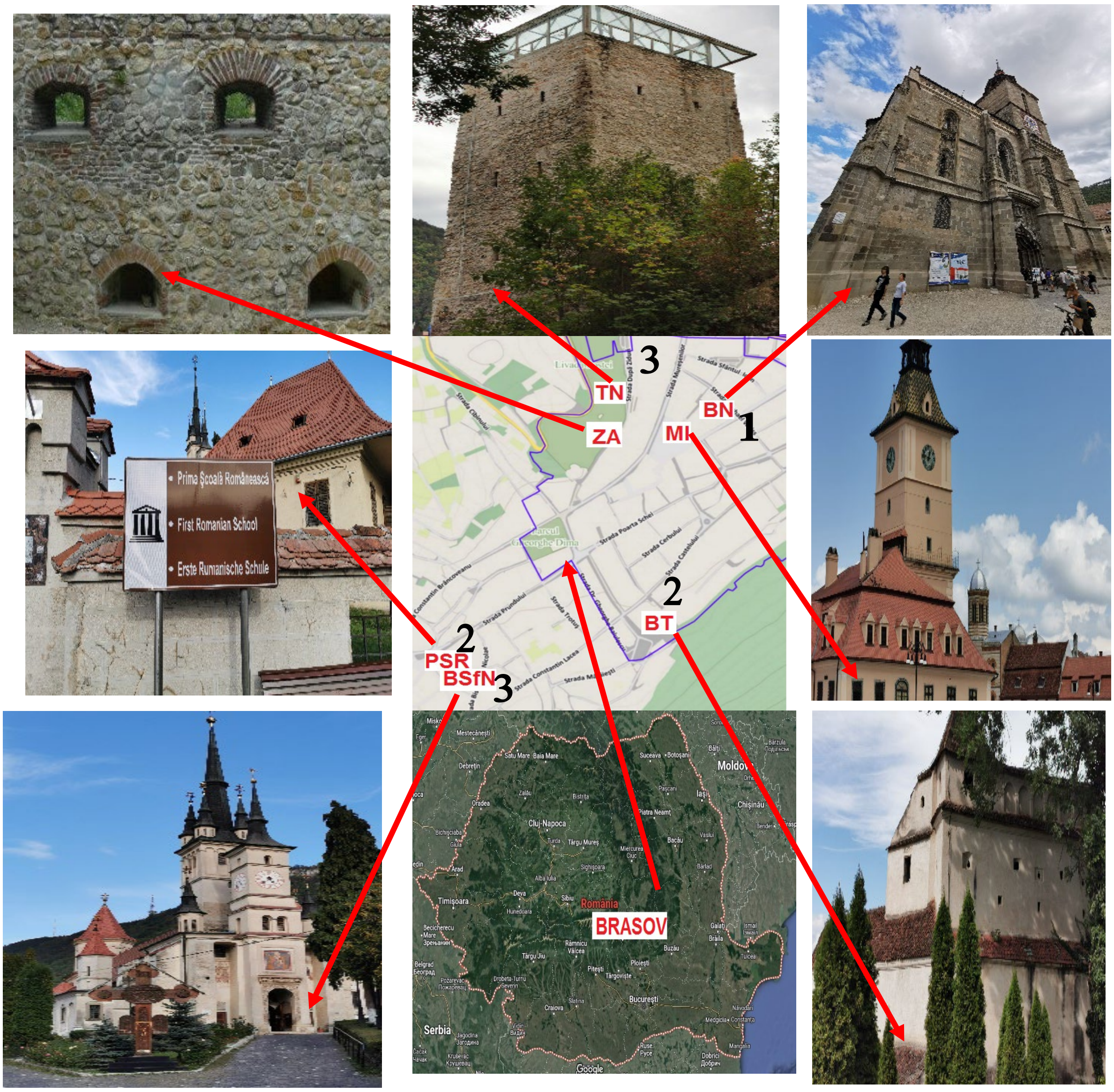


Figure 2. Sampled heritage buildings in the city of Braşov, Transylvania, Romania: First Romanian School (PSR); History Museum (MI); Black Church (BN); St. Nicholas Church (BSfN); Medieval Fortress Wall (ZA); Weavers' Bastion (BT); Black Tower (TN) (Photos personal archive August 2022).

1- central pedestrian area, 2- low traffic area, 3- central high traffic area

CHAPTER 5. AIR POLLUTION IN THE CITY OF BRAȘOV

5.1. Introduction

Access to clean air is a fundamental human right that is still insufficiently respected globally. According to studies, there is no safe level of air pollution; even minimal concentrations (e.g. below 5 $\mu g/m^3$ of $PM_{2.5}$) can carry significant mortality risks [10].

The specific objective of this chapter was to determine pollutant concentrations in the vicinity of the monuments selected for study. The main aim was to analyse in detail the impact of these pollutants on the degradation process of the monuments. By measuring and quantifying the levels of pollutants, this study aims to provide a clear insight into the environmental factors that accelerate the deterioration of historic structures.

5.2. Determination of air composition around monuments

The observations indicate a distinct trend in the variations of the concentrations of the four compounds analysed (benzene, toluene, xylenes and terpenes), which remains constant for all of them. It can be seen that around midday the concentrations of organic pollutants can be up to five times higher than those recorded in the early morning hours, a trend that reverses towards the evening. Even if the levels of pollutants do not exceed standard limits, their visible presence in the vicinity of the two monuments indicates specific sources of pollution. These sources include car traffic, which not only passes through the area, but also includes vehicles supplying local traders, as well as the heating systems of the buildings. These activities affect both the state of conservation of monuments and public health. For example, comparative studies show that BTEX concentrations similar to those in the vicinity of monuments have been recorded in urban areas such as Bandar Abbas, Iran, where the average was 18.00 $\mu g/m^3$, with variations between 5.21 and 67.24 $\mu g/m^3$, [11] and in peri-urban areas such as Orléans, France, with a concentration of 3.47 $\mu g/m^3$ [12]. These data suggest that urban pollution can reach comparable levels in different geographical contexts.

Furthermore, the ratio between toluene and benzene concentrations was 1.19 ± 0.12 for the Black Church and 1.44 ± 0.27 for the Black Tower, indicating a predominance of stationary sources of pollution, such as residential heating, compared to transportation. This finding is supported by studies such as those carried out [13], which analysed the impact of different urban pollution sources and their effects on cultural heritage.

5.3. Monitoring pollutant concentrations in Brașov

Since point measurements of pollutant concentrations around monuments in Brașov were not possible, it was decided to use the measurements recorded by two monitoring stations in Brașov (BV2 and BV3 located near the medieval structures).

Over 14 years in Brașov, pollutant concentrations remained relatively unchanged. PM_{10} and carbon oxides were low, but NO_2 and SO_2 often approached legal limits, raising environmental and public health concerns. NO_2 and SO_2 mainly originate from fossil fuel combustion, which is intense in and around urban areas due to traffic, industrial and culinary activities [14, 15]. In an extensive study for Bejing, China it was shown that NO_2 air concentrations showed a linear increase towards the city center, while such a spatial pattern was not observed for SO_2 [16]. Variations in particulate matter (PM) levels were caused by domestic and industrial emissions, which were quite high and observed as a common phenomenon. Garaga et al [17] found higher annual mean PM concentrations at a monitoring point near a four-way intersection (220 ± 23 µg/m^3), followed by a single-traffic street (167 ± 21 µg/m^3) and an industrial area (161 ± 23 µg/m^3). Also, Hama et al [18] found the highest four-year annual mean concentrations at a mixed location (179 ± 99 µg/m^3) compared to residential areas in Delhi, due to the influence of a variety of sources near the sampling site. However, such concentrations are not found in Brașov, with PM concentrations not exceeding 50 µg/m^3.

5.4. Conclusions

Global access to clean air is still a major problem, particularly affecting historic monuments and buildings. In dense urban areas, where human activities such as traffic and urban heating are prevalent, air pollution often reaches levels that not only exceed World Health Organisation standards, but also affect the structural integrity and aesthetics of historic buildings. Pollutants such as fine $PM_{2.5}$ particles, even in apparently minimal concentrations, have the ability to penetrate the porous materials of monuments, accelerating degradation and corrosion processes. These effects are not only visible, but can lead to irreversible damage that complicates conservation efforts.

In addition, weather conditions and the specific urban layout of each city can inhibit the efficient dispersion of these pollutants, creating an environment in which acids formed from the reaction of pollutants with atmospheric moisture can persist and intensify the degradation of stone, metals and other building materials. Thus, the importance of continuous monitoring and implementation of effective pollution abatement policies becomes evident, not only for the protection of public health, but also for the preservation of architectural heritage. The adoption of integrated strategies, combining air filtration and purification technologies with conservative restoration of affected buildings, is essential to maintain their historical and cultural value in the long term. These efforts need to be supported by advanced research and tailored to local specificities to optimise the effectiveness of interventions in the dynamic context of climate change and accelerated urbanisation.

CHAPTER 6. INFLUENCE OF AIR POLLUTANTS ON BRICKS IN MEDIEVAL HERITAGE BUILDINGS OF BRAȘOV

6.1. Introduction

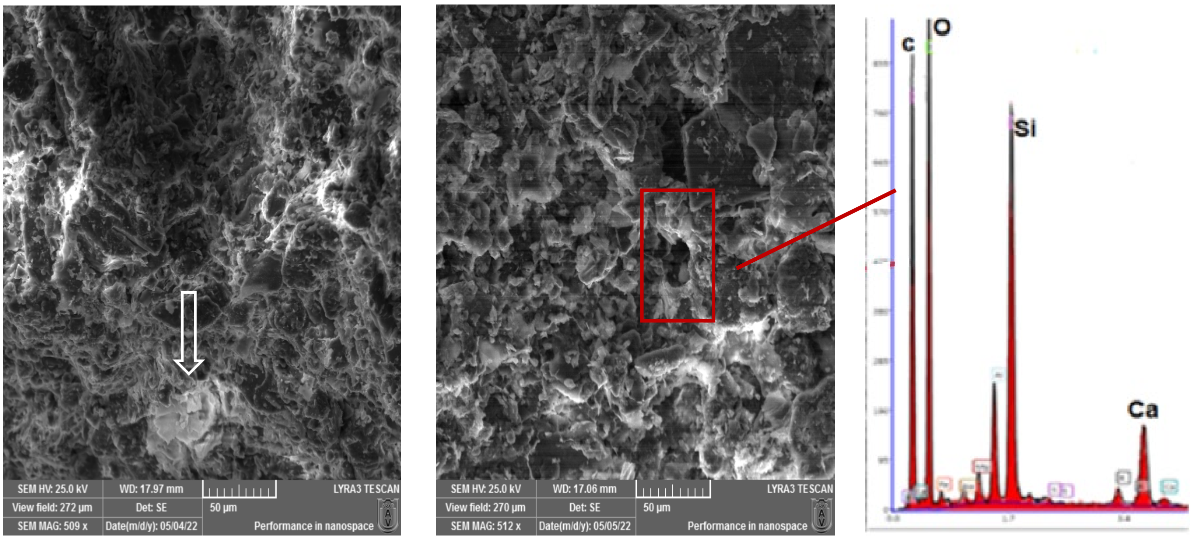
Buildings of cultural and historical importance around the world attract large numbers of tourists every year, leading to overcrowding. This influx of visitors increases urban vehicle traffic, exacerbating the demands of tourist travel. When combined with emissions from local industries and the influences of nearby agricultural activities, these factors collectively contribute to urban air quality degradation. The resulting air pollution not only endangers the structural integrity and aesthetic value of these historic buildings, but also poses health risks to the dense crowds that visit them [19]. This situation emphasizes the urgent need for holistic strategies for air quality management and cultural heritage preservation in urban environments. The objective of this chapter has been to study the impact of pollutants on bricks in the 7 chosen locations presented in detail in Chapter 4 [20].

6.2. FTIR-ATR analysis of brick samples

The FTIR-ATR spectra of the samples from the inner part of the bricks (PSR-I, MI-I, BN-I, BSfN-I, ZA-I, BT-I, TN-I) reveal the presence of specific vibrational bands of silicates, phyllosilicates, feldspars, carbonates and anhydrous clay minerals, in agreement with the results obtained from the XRD analysis. The calcite band recorded at ~1430 cm^{-1} occurs at a distance from the main silicate band recorded in the range 1300-900 cm^{-1}. The specific IR bands of carbonates and silicates provide essential information about the mineralogy of the brick samples, including the firing temperature [21].

6.3. SEM-EDX analysis of brick samples

The morphology of weathering crusts on the surface of bricks and their chemistry were investigated by scanning electron microscopy coupled with energy dispersive X-ray diffraction (SEM-EDX).



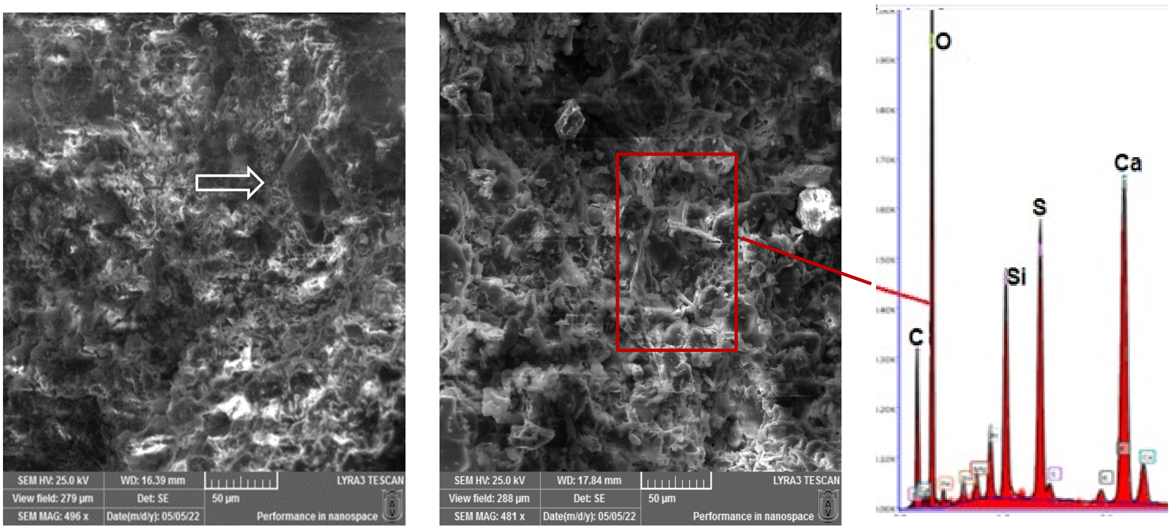


Figure 3. SEM images and EDX spectra of chemically weathered crust: (a) PSR-E - Dilute calcite crystals in white crust (efflorescence); (b) BN-E- White crust with porous structure and large crystals of reprecipitated CaCO$_3$; (c) ZA-E- Black crust with embedded halite crystals; (d) BSfN-E - Black crust with acicular gypsum crystals on matrix of reprecipitated CaCO$_3$.

Some representative SEM images of the black and white crust are shown in Figure 3, together with EDX spectra of the investigated areas.

6.4. X-ray diffraction analysis of brick materials

X-ray diffraction (XRD) analysis was used to characterize the mineralogical composition of the samples from the inner part of the investigated burnt bricks and to estimate the firing temperatures used in the manufacturing processes. The main mineralogical classes identified were silicates, phyllosilicates, K-feldspars and plagioclase feldspars. Small amounts of carbonate and clay minerals (anh.) were also observed. The presence of calcite and orthoclase confirms the estimated firing temperature for samples PSR-I, MI-I, BN-I and BSfN-I, with the possibility that sample BSfN-I (with the highest calcite content) was fired slightly lower than the others.

6.5. Thermogravimetric analysis of brick samples

The thermogravimetric studies demonstrated, over the temperature range 30-10000 ˚C, a high thermal stability of the samples taken from the inner side of the bricks (BSfN-I, TN-I). Only in the case of sample BSfN-I a small mass loss of $\Delta m = 0.36\%$ was observed in the range 318-4520˚C, with a maximum rate at T_{DTG}=3400˚C, probably due to the removal of rehydration water over time of kaolinite, whose presence in the mineralogy of the material was identified by XRD and FTIR-ATR analysis. This behaviour has been reported in the literature in a number of studies related to the metakaolinite rehydration phenomenon in kaolinite [22-25]. In the case of the TN-I sample, no mass loss stage was recorded over the thermal range 30-10000˚C, confirming that the temperature at which this brick was fired was above 10000˚C, as determined by mineralogical analysis based on XRD results (~1100˚C).

6.6. Analysis by gas chromatography coupled with mass spectrometry of organic deposition of brick samples

Numerous studies have demonstrated that microorganisms influence the degradation of brick by various mechanisms, including decomposition of organic and bioorganic matter, resulting in the formation of carboxylic acids; direct mineral decomposition; generation of metabolic products such as oxalates; forcing cavities and cracks; and direct involvement in the crystallization of salts (e.g., bacteria can precipitate calcite and other minerals). According to Comite et al. [26], calcium oxalate on ancient brick surfaces usually results from partially oxidizing organic carbon, which can be attributed to degradation of organic structures, biological activity, or exposure to atmospheric pollutants.

Nonadecane has a significant presence in all samples, but is predominant in the indoor samples, which may indicate a reduced degradation process in the absence of direct exposure to external factors. Interestingly, docosane and hexacosane are almost non-existent in most of the samples, except in the outer ZA, where docosane reaches a notable value of 14.86% and hexacosane reaches 22.78%. This discrepancy can be explained by specific peculiarities of the external environment or by a specific biological activity in that zone. In conclusion, the analysis of the chemical composition of hexane extracts in bricks from various medieval monuments shows significant differences between indoor and outdoor samples, influenced by environmental factors and the presence of biocrust.

6.7. Conclusions

The studies carried out highlight the influence of air pollutants on the bricks in the medieval heritage buildings of Brașov, emphasizing that the large influx of tourists and intensified urban traffic contribute to air pollution, negatively affecting the structural and aesthetic integrity of these buildings. The main pollutants, such as sulphur dioxide, nitrogen oxides, chlorides, carbon dioxide and ozone, cause significant deterioration, manifested by loss of mass, changes in porosity, discoloration and embrittlement. Damage mechanisms include dry and wet deposition of pollutants, which accelerate erosion and structural weakening of materials. FTIR-ATR analysis of the brick samples revealed the presence of vibrational bands specific to silicates, phyllosilicates, feldspars, carbonates and anhydrous clay minerals, indicating variations in mineralogical composition and firing temperature. The differences between the inside and outside samples reflect the influences of the external environment, with the exterior samples showing higher amounts of carbonates and signs of moisture. SEM-EDX-EDX analysis revealed the presence of bio- and and pollution on the surface of the bricks, the black crusts being composed mainly of gypsum and calcite crystals, and the biocrust containing organic filaments and calcium oxalate crystals. XRD analysis allowed the estimation of the firing temperatures of the bricks, indicating variations from 800°C to 1100°C, and samples fired at higher temperatures show different mineralogical compositions, including the formation of high-temperature minerals such as anorthite and wollastonite. The external environment plays a crucial role in the accumulation of organics and minerals on the surface of the bricks, and the external samples contain higher concentrations of compounds such as hexadecane and octadecane, indicating a significant influence of atmospheric pollutants on the building materials.

CHAPTER 7. THE IMPACT OF POLLUTION ON MORTAR IN THE MEDIEVAL HERITAGE BUILDINGS OF BRAȘOV

7.1. Introduction

Mortar is a main building material consisting of an inactive element called aggregate, which is usually a combination of sand and gravel. It is bound together by cement and water. Throughout history, many civilizations have used a variety of materials for binding purposes. The distinctive characteristics of concrete are determined by the specific type of cement used, the admixtures incorporated and the relative proportions of cement, aggregate and water [27]. Detrimental effects of sulphate corrosion include swelling, cracking, spalling, exfoliation, increased permeability and loss of strength due to chemical and physical processes. Sulfate corrosion can be usually classified into five types based on the corrosion products: ettringite corrosion [28], gypsum corrosion [29], taumasite corrosion [30, 31], crystalline physical erosion of sulfates [32] and dealuminization and decalcification of C-S-H gels [33].

7.2. FTIR-ATR analysis of mortar samples

The technique of FTIR analysis is commonly used to characterize the composition of ancient mortars because it allows rapid identification of the materials in the samples and weathering compounds and in combination with thermogravimetric analysis (TG/DTG) can provide fairly accurate data on the percentage content of each component [34, 35].

In all the analyzed samples specific curation bands were identified, which proves that the aggregates used for the preparation of the mortars were sand-based. Thus, the asymmetric stretching vibration of the (Si-O) bond in quartz was recorded in the range 978 cm^{-1} - 1036 cm^{-1}, and the symmetric stretching vibration at ~795 cm^{-1}. The deformation vibration of the (Si-O) structure in the curate was observed at ~695 cm^{-1} while the vibrational bands of the (Si-O-Si) cluster were recorded at ~778 cm^{-1} and ~647 cm^{-1}.

In the case of mortar samples taken from the external areas of the medieval buildings investigated, areas that were subject to the action of acidic atmospheric pollutants (e.g. SO_3, acid rain), in addition to the bands specific to the aggregates and binders used in their preparation, some vibrational bands specific to weathering compounds were also observed. Thus, in the FTIR-ATR spectra for the BSfN-E sample, taumazite ($CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) specific bands were obtained, located at 3534 cm^{-1} (O-H bond stretching vibration), 1620 cm^{-1} (O-H bond deformation vibration in crystallization water molecules) and 675 cm^{-1} specific to the $(SO_4)^{2-}$ group stretching vibration. According to literature data, taumazite is an expansive mortar degradation compound that forms over time due to the action of dry and wet acid deposition on calcium carbonate and C-S-H gel [35, 36].

7.3. SEM-EDX analysis of building mortar samples

Scanning electron microscopy (SEM) provides a detailed view of microstructural changes and degradation processes in mortar, which is crucial for understanding its long-term behavior under the influence of environmental factors such as pollution and acid rain. The main hydration product, calcium silicate hydrate (C-S-H), forms a gel-like matrix that encapsulates the cement particles, contributing significantly to the mechanical strength and durability of the mortar. This matrix is integral to the structural integrity of the mortar, ensuring the cohesion and robustness of the building material.

Calcium hydroxide, another significant by-product of cement hydration, although less critical to structural strength, plays a vital role in mortar chemistry. It undergoes carbonation, reacting with carbon dioxide in the air to form calcium carbonate, a process that can increase the hardness and density of mortar over time. However, this component is susceptible to dissolution by acidic solutions such as acid rain. When acid rain penetrates the mortar, it can dissolve the calcium hydroxide and weaken the protective calcium carbonate layer, leaving the C-S-H matrix exposed to further degradation. Furthermore, acid rain can introduce sulfates into the mortar, which can react with the existing calcium hydroxide to form secondary ettringite. Unlike ettringite which forms during the initial hydration process and contributes to the early strength of the concrete, this secondary formation can occur at later stages if the mortar is exposed to external sources of sulfates. This delayed ettringite formation can be problematic as it typically leads to expansion in the mortar, causing internal stresses that can result in cracking and increased porosity. These effects compromise the structural integrity of the mortar and reduce its service life.

SEM analysis is particularly valuable in detecting these processes because it can provide high-resolution images that reveal the presence of cracks, voids and specific morphological changes in the hydration products. By identifying these changes, SEM helps diagnose the degree of deterioration and understand the impact of the environment on the mortar. This information is essential for developing more sustainable mortar formulations and implementing protective measures to protect existing structures from environmental damage.

7.4. Analysis by gas chromatography coupled with mass spectrometry of organic deposits of mortar samples

However, there are differences between indoor and outdoor mortar samples due to the formation of an organic biocrust substrate. Comparison of the chromatograms obtained from the inside and outside samples of the Black Tower (NT) shows a higher amount of organics in the exterior compared to the interior (Figure 4). Specifically, compounds such as hexadecane and octadecane are present in higher concentrations in the exterior samples compared to the interior. This suggests that external environmental factors contribute to the accumulation of these substances.

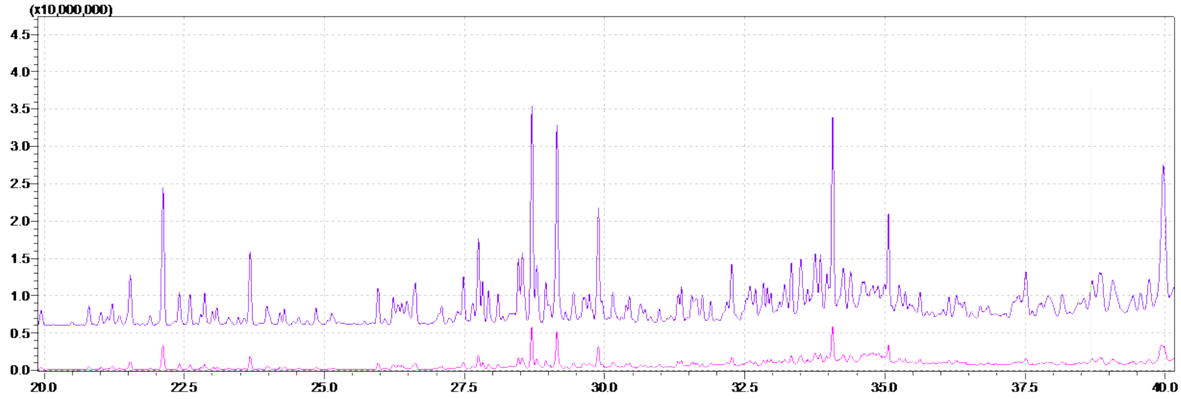


Figure 4. Overlay of chromatograms for Black Tower mortar extracts from the inside (TN-I ------pink) versus outside (TN-E -------blue), highlighting significant differences in chemical composition due to exposure to external environmental factors.

It can be seen that nonadecane has a significant presence in all samples, but is predominant in the interior samples, which may indicate a reduced degradation process in the absence of direct exposure to external factors. Interestingly, docosane and hexacosane are almost non-existent in most of the samples, except in the exterior samples of monument ZA, where docosane reaches a notable value of 14.86% and hexacosane reaches 22.78%.

This discrepancy can be explained by specific peculiarities of the external environment or by a specific biological activity in that area. It is also evident that the concentrations of tridecane and tetradecane are higher in the outdoor samples than in the indoor samples, suggesting continuous external contamination.

7.5. Conclusions

The study demonstrated that air pollution has a significant impact on the durability and integrity of mortars in medieval heritage buildings in Brașov. FTIR-ATR analyses revealed the presence of calcium carbonate in the mortars in the inside areas of the buildings, indicating the use of hydrated lime as the main binder. External samples showed weathering compounds such as thaumazite, indicating significant chemical degradation caused by atmospheric pollutants. SEM-EDX-EDX analysis revealed microstructural and chemical changes in the mortars exposed to pollution, with the formation of secondary ettringite causing expansion, cracking and increased porosity, reducing structural integrity. The different elemental composition between internal and external samples highlights the environmental impact on mortar durability.

Gas chromatography coupled with mass spectrometry showed significant differences in the chemical composition of the organic deposits between internal and external samples, with higher concentrations of organic compounds such as hexadecane and octadecane in the external samples, suggesting an accumulation influenced by external environmental factors. The presence of tridecane and tetradecane in higher concentrations in the external samples indicates continuous contamination from the external environment. These findings underline the role of air pollution in altering the chemical composition of building materials and emphasize the need for tailored conservation strategies to protect cultural heritage. The study highlighted the importance of detailed analysis for understanding degradation processes and developing more sustainable mortar formulations, as well as implementing protective measures to prolong the life of historic buildings in the face of modern environmental factors.

GENERAL CONCLUSIONS

Global access to clean air is still a major problem, particularly affecting historic monuments and buildings. In dense urban areas, where human activities such as traffic and urban heating are prevalent, air pollution often reaches levels that not only exceed World Health Organization standards, but also affect the structural integrity and aesthetics of historic buildings. Pollutants such as $PM_{2.5}$ fine particulate matter, even in seemingly minute concentrations, have the ability to penetrate into the porous materials of monuments, accelerating the processes of degradation and corrosion. These effects are not only visible but can lead to irreversible damage that complicates conservation efforts. In addition, weather conditions and the specific urban layout of each city can inhibit the efficient dispersion of these pollutants, creating an environment in which acids formed from the reaction of pollutants with atmospheric moisture can persist and intensify the degradation of stone, metals and other building materials. Thus, the importance of continuous monitoring and implementation of effective pollution abatement policies becomes evident, not only for the protection of public health, but also for the preservation of architectural heritage. The adoption of integrated strategies, combining air filtration and purification technologies with conservative restorations of affected buildings, is essential to maintain their historical and cultural value in the long term. These efforts need to be supported by advanced research and tailored to local specificities to optimise the effectiveness of interventions in the dynamic context of climate change and accelerated urbanisation.

The studies carried out highlight the influence of air pollutants on the bricks in the medieval heritage buildings of Brașov, emphasizing that the large influx of tourists and intensified urban traffic contribute to air pollution, negatively affecting the structural and aesthetic integrity of these buildings. The main pollutants, such as sulphur dioxide, nitrogen oxides, chlorides, carbon dioxide and ozone, cause significant deterioration, manifested by loss of mass, changes in porosity, discoloration and embrittlement. Damage mechanisms include dry and wet deposition of pollutants, which accelerate erosion and structural weakening of materials. FTIR-ATR analysis of the brick samples revealed the presence of vibrational bands specific to silicates, phyllosilicates, feldspars, carbonates and anhydrous clay minerals, indicating variations in mineralogical composition and firing temperature. The differences between the inner and outer samples reflect the influences of the external environment, with the outer samples showing higher amounts of carbonates and signs of moisture. SEM-EDX analysis revealed the presence of bio- and anopollution on the surface of the bricks, the black crusts being mainly composed of gypsum and calcite crystals and the biocrust containing organic filaments and calcium oxalate crystals. XRD analysis allowed the estimation of the burning temperatures of the bricks, indicating variations from 800°C to 1100°C, and samples burned at higher temperatures show different mineralogical compositions, including the formation of high-temperature minerals such as anorthite and wollastonite. The external environment plays a crucial role in the accumulation of organics and minerals on the surface of the bricks, and the external samples contain higher concentrations of compounds such as hexadecane and octadecane, indicating a significant influence of atmospheric pollutants on the building materials.

The study showed that air pollution has a significant impact on the durability and integrity of mortars in medieval heritage buildings in Brașov. FTIR-ATR analyses revealed the presence of calcium carbonate in mortars in the inside areas of the buildings, indicating the use of hydrated lime as the main binder. External samples showed weathering compounds such as thaumazite, indicating significant chemical degradation caused by atmospheric pollutants. SEM-EDX analysis revealed microstructural and chemical changes in mortars exposed to pollution, with the formation of secondary ettringite causing expansion, cracking and increased porosity, reducing structural integrity. The different elemental composition between internal and external samples highlights the environmental impact on mortar durability. Gas chromatography coupled with mass spectrometry showed significant differences in the chemical composition of the organic deposits between internal and external samples, with higher concentrations of organic compounds such as hexadecane and octadecane in the external samples, suggesting an accumulation influenced by external environmental factors. The presence of tridecane and tetradecane in higher concentrations in the external samples indicates continuous contamination from the external environment. These findings highlight the role of air pollution in altering the chemical composition of building materials and emphasize the need for tailored conservation strategies to protect cultural heritage. The study highlighted the importance of detailed analysis for understanding degradation processes and developing more sustainable mortar formulations, as well as implementing protective measures to prolong the life of historic buildings in the face of modern environmental factors.

An integrated approach combining continuous pollution monitoring, the use of sustainable building materials and the implementation of effective pollution reduction policies could prolong the life and preservation of Brașov's cultural heritage.

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