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Measurement of volatile organic compounds (VOCs) in libraries and archives in Florence (Italy)

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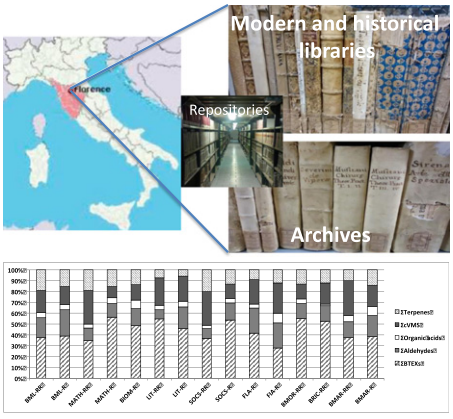
HIGHLIGHTS

- VOCs measurements in archives and libraries in Florence (Italy)
- BTEX were the most abundant VOCs.
- High concentrations of acetic acid were determined in archives and libraries.
- Furfural, markers of paper degradation, was constantly present.
- Libraries and archives located in urban areas are influenced by outdoor sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Indoor air samples from libraries and archives in Florence, Italy, were collected and analysed for a variety of volatile organic compounds. The aim was to perform a characterisation of the indoor air quality, and try to elucidate if there are VOCs that may cause or result from the determination of the cultural heritage institutions.
All compounds of interest were regularly detected, with BTEXs (Benzene, Toluene, Ethylbenzene, Xylenes) being the most abundant and followed by cyclic volatile methylsiloxanes, aldehydes, terpenes and organic acids. The prevalence and qualitative characteristics, such as concentrations, profiles and indoor/outdoor ratios of BTEXs underline the important influence of the outdoor air infiltrations on the indoor air concentrations. Acetic acid that is a substance that can oxidise books and other exposed objects was detected at concentrations ranging between 1.04 and 18.9 μg m^{-3}, while furfural, that is a known marker of paper degradation, was constantly present at concentrations that ranged between 5.26 and 32.6 μg m^{-3}.
This work shows the importance that indoor air quality monitoring campaigns can have in order to give early warning to cultural heritage institution managers about the impact that indoor air quality can have on exposed and/or preserved objects.

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1. Introduction

Cultural heritage institutions (CHIs) (libraries, archives, museums, galleries, cultural centres and historic houses) have for storage and exposition important articles/objects, which attract the interest of visitors, and as such, the need to preserve their value of their assets becomes imperative. In particular, historical and modern libraries and archives house large numbers of book collections and documents made of a wide range of organic materials, including cellulose- (i.e. paper, some textiles wood), synthetic- (i.e. book, cover material) and other organic materials representing a minor amount of text-carrier (i.e. silk). They also house a large amount of writing/printing/drawing material (i.e. dies, inks, pigments, binders, glues) of which texts and images are produced. These materials undergo a continuous and inevitable deterioration due to natural ageing, or due to contact with corrosive, oxidising, or acidic agents etc. Generally, the preservation measures taken by the Authorities consist in controlling environmental factors such as temperature, relative humidity, light sources, biological infestation, air renewal and by assuring good air circulation (Walch, 1990). To go one step further, in the last years, there is an increasing interest in studying the impact that the air pollutants can have on exposed articles, including both outdoor-originated and indoor-emitted air pollution.

The major outdoor pollutants that can pose risks to cultural property are sulphur dioxide, ozone, nitrogen dioxide, reduced sulphur gases, such as hydrogen sulphide, and certain volatile organic compounds (VOCs). The occurrence of VOCs in indoor environments can be governed by external sources, including vehicular traffic, industrial fumes, but also indoor sources. The latter include outgassing from building and/or decorative materials (i.e. floor and wall covering, carpet, insulation), solvent based paints, products used for the maintenance and the cleaning (i.e. detergents, insecticides etc.), heating and air conditioning plants, human activities and finally, emissions from the exposed items (Baer and Banks, 1985). In addition, to the main concern that indoor air pollution can adversely impact the human health, in CHI environments it may also accelerate processes that can damage important museum collection items (e.g. oxidation and hydrolysis in books, documents and collection materials in general, discoloration and other degradation effects). As a consequence of the exposed items degradation, VOCs can also be formed from the paper itself, giving rise to the memorable smell of old books (Gibson et al., 2012).

The most common indoor generated VOCs related to libraries and archives are, acetic acid, formic acid, furfural, 4-hydroxy benzoic acid, 4-hydroxy acetophenone (Tétreault, 2003; Salthammer et al., 2010), which have been attributed to lignin or cellulose degradation (Gibson et al., 2012) and, for this reason, suggested as chemical deterioration markers.

Florence is one of the most visited cities in Italy and this is partially thanks to its very important cultural heritage and number of important cultural heritage institutions. In particular, academic and historical libraries and archives in Florence (Italy) house medieval manuscripts, incunabula, rare books, atlases and maps, music manuscripts, personal documents of famous individuals as well as antique and modern academic books, representing one of the most important book patrimonies and a valuable written cultural heritage of the Italian State that needs to be preserved and conserved. To this end, the objectives of this study, carried out in collaboration with librarians and special collection curators, were to investigate, for the first time, the indoor air quality at selected locations inside Florentine libraries and archives and to try to elucidate if there are VOCs that may cause or result from the deterioration of the CHI objects. Finally, the impact of outdoor air pollution and the relation with the indoor air quality was studied.

2. Experimental

2.1. Monitoring locations

Modern libraries, historical-type libraries and historical archives located in Florence (Italy) were the sampling sites of interest. A total of 48 air samples were collected in reading rooms and repositories in eight libraries and two historical archives in Florence (Italy) (Table 1). In particular, four modern university libraries (Literature (LIT), Mathematics (MATH), Biomedics (BIOM) and Social Sciences (SOCS) and four historical libraries located in the city centre were included in the study. Historical libraries included: - Biblioteca Medicea Laurentiana (BML), which is considered as having the most important and prestigious collection of antique books in Italy. It comprises the most lasting cultural inheritance which the Medici family has passed to the attention care and admiration of posterity, including rare manuscripts of scientific nature; - Biblioteca Marucelliana (BMAR), which possesses an important heritage made up of over 500,000 volumes (including incunabula and sixteenth-century editions), manuscripts and unbound papers (autograph works and correspondence of literary, historic, artistic and scientific interest), periodicals and opera libretti, in addition to an important collection of prints and drawings (15th to 19th centuries); - Moreniana (BMOR) library, located in Palazzo Medici Riccardi, which houses an exceptional book patrimony on the history of Florence, and Biblioteca Riccardiana (BRIC), which houses an exceptional book patrimony which is equipped with a complex system of wooden shelves, carved and gilded in the 18th century. The historical archives were located in Florence (FLA) and Fiesole (FIA) and host documents, topographic maps, drawings and publications.

The location of the sampling sites within the city of Florence is reported in Fig. 1.

2.2. Sampling and analysis

Between May and June 2015, air samples were collected in different locations of eight libraries and two archives located in Florence (Italy). VOCs sampling and analysis were carried out as previously described with minor modifications (Pieri et al., 2013; Katsoyiannis et al., 2014). Briefly, prior to air sampling, the tubes, containing Tenax GR (35/60 mesh) and Graphitized Carbon Black, were conditioned at 320 °C for 120 min, then at 335 °C for 30 min with a 100 ml min^{-1} reverse flow of high purity (99.999%) Helium (as in EPA method TO-17, USEPA 1997), whereas the pocket pumps were calibrated at 200 ml min^{-1}. The tubes were sealed, stored at +4 °C until the analysis.

Acetic acid and Formic acid were adsorbed on tubes containing Tenax TA (35/60 mesh), carbograph 1TD (40/60 mesh) and carboxen 1003 (40/60 mesh), conditioned at 100 °C for 15 min, then at 200 °C for 15 min then at 300 °C for 15 min and finally at 350 °C for other 15 min.

Air samples were taken at a height of approximately 1.5 m above the floor in the centre of the sampled room. Three air samples were collected for each sampling site and the concentrations average has been reported. To compare indoor with outdoors samples, the corresponding environment was also monitored for the same pollutants. Outdoor samples were also taken simultaneously near the vicinity of the building.

Table 1
Description of sampling locations.

Sampling sites			Acronym	Locations and number of samples	
				Reading Room (RR)	Repository (R)
Modern-type	Academic libraries (AL)	Literature	LIT	1	2
		Mathematics	MATH	2	1
		Biomedics	BIOM		4
		Social sciences	SOCS	3	2
Historical-type (historical libraries, HL)	Biblioteca Medicea Laurentiana		BML	2	4
	Biblioteca Marucelliana		BMAR	4	4
	Biblioteca Moreniana		BMOR	4	
	Biblioteca Riccardiana		BRIC	4	
Historical archives (HA)	Florence		FLA		7
	Fiesole		FIA		4