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Original article

Pollutants monitoring and air quality evaluation in a confined environment: The 'Majesty' of Ambrogio Lorenzetti in the St. Augustine Church in Siena (Italy)

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ABSTRACT

A monitoring campaign of the levels of some organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), perfluoro alkylated substances (PFASs), chlorinated pesticides (4 isomers of hexachlorocyclohexane, hexachlorobenzene, 6 isomers and metabolites of DDT and dieldrin), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs), in different matrices (dust taken from the floor and under a wall painting and fragments of the 'Majesty' wall painting by Ambrogio Lorenzetti), was conducted in the historical museum of St. Augustine's church in Siena (Italy). Instrumental analyses were made by gas chromatography and liquid chromatography coupled with mass spectrometry. The results showed the presence of some organic pollutants (PAHs and PBDEs), whose interaction with the surfaces of works of art are not yet fully elucidated. The study was complemented by monitoring the air quality inside and outside the church for the detection of volatile organic compounds (VOCs); all the results showed low levels of air pollution.

1. Introduction

Over the past few years, there has been a growing interest by the scientific community to issues related to cultural heritage pollution, both in urban areas and inside museums (Camuffo et al., 2001; Bonazza et al., 2005; Schieweck et al., 2005, 2007; Nava et al., 2010). Most studies have focused on inorganic pollutants, such as ozone, sulfur dioxide and nitrogen dioxide (Kucera and Fitz, 1995; Screpanti and De Marco, 2009), whilst less attention has been put on the contamination due to organic compounds in artistic artifacts, historical buildings and museums (Schieweck et al., 2005; Marcotte et al., 2014). The potential sources of indoor pollution are various, such as building materials and equipment, products for cleaning, conserving and restoring, bio-contaminants, outdoor pollution, and combustion processes (Khalequzzaman et al., 2007). Moreover air pollution, both from industrial sources and from vehicular traffic, generates degradation, not only in the artistic heritage present in the urban environment (statues, monuments, historic buildings, archaeological sites), but also in the artifacts kept in museums or churches. The micro-climatic conditions, the pressure of tourism and the structural characteristics of the buildings must be added to the external factors together with all factors that affect the exchange of indoor–outdoor pollutants and the emission of substances such as flame retardants and biocides, from furniture and upholstery held indoor.

This work is part of a measurements campaign performed within the SICAMOR project (Development of Chemical Investigations Applied for Maintenance and Restoration of Art works). The project concerned the characterization of trecentist Sienese operas, such as the wooden panels 'Adorazione dei Magi' (Marchettini et al., 2013), by Bartolo di Fredi and 'Madonna with Child' (Atrei et al., 2014), attributed to Pietro Lorenzetti, the Ambrogio Lorenzetti's older brother, both disappeared in 1348.

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In this work we investigate the air quality and the environmental conditions of the place where the well-known wall painting 'The Majesty' (1337–1338, Fig. 1) by Ambrogio Lorenzetti is located. In previous works we already characterized the chemical composition of the pigments (Damiani et al., 2014) and the ligands (Benetti et al., 2015) used in the *secco* colors of 'The Majesty'.

'The Majesty' is located in the thirteenth-century Church of St. Augustine, in the center of the city of Siena (central Italy), together with other important art works: a polyptych by Simone Martini, a painting by Perugino, wall paintings by Francesco di Giorgio and Luca Signorelli. Even though the church is located in a "traffic limited area", the traffic is quite intense because of the public transportation, private residents cars and many commercial activities.

In this work, in particular, we are interested in assessing the presence and the fate of emergent indoor pollutants, such as polybrominated diphenyl ethers (PBDEs), in touristic locations and cultural heritage places, potentially having many visitors per year. To assess the level of pollution inside the church, we monitored some organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides (OCPs), polychlorinated biphenyls, (PCBs), perfluoroalkilated compounds (PFASs) and polybrominated diphenyl ethers (PBDEs) in different matrices: fragments from plaster frame of the "Majesty", fragments of plaster from the nave columns, dust samples "dusting" below the fresco and samples of dust from the floor of the church.

Moreover, diffusive samplers were placed inside the church, in the surroundings and in other areas of the city of Siena to find possible correlations with the external environment and to assess the origin of the pollutants.

Diffusive samplers having a radial symmetry for a high sampling rate, have been successfully employed for monitoring common pollutants concentration in atmosphere (Cucciniello et al., 2012, 2013; Proto et al., 2014) and particularly BTEX, i.e. benzene, toluene, ethylbenzene and xylenes (Ilgen et al., 2001), the most common among the volatile organic compounds generally present in a polluted environment. Diffusive (or passive) samplers, initially developed for the air monitoring of small workplaces, have been found to be useful and cost-effective alternative to conventional pumped samplers, even for the atmospheric sampling and monitoring. In particular, they are preferred when the average (in space and time) concentrations, instead of the real time, are required for the purpose of the monitoring (Gorecki and Namiesnik, 2002; Seethapathy et al., 2008).

2. Materials

2.1. Pollutants sampling methods

Due to the limited quantity of some samples, in few cases only PAHs were analyzed. To have a better picture of the origin of the pollutants inside the church, parallel analysis were performed on samples coming from other locations, namely from the Pinacoteca di Siena, a protected area located few hundreds meters from the church, from private homes in the center of Siena and from a private home in the Sienese countryside (Pacina). A complete list of the samples is presented in Fig. 1 (samples 1–3) and in Table 1 (samples 4–24).

List of the samples analyzed:

- St. Augustine's Church: 2 wall painting dusting (right and left), 2 wall painting frame (upper and lower) and 1 wall painting fragment, 2 floor dust (nave and Cappella Piccolomini). In Fig. 1 the sampling points collected by the "Majesty" wall painting are reported.
- Samples from other locations in Siena, for comparison: 4 house dust, 3 Siena center, 1 from sienese country; from Pinacoteca fragments by following: 1 from the wooden frame of the painting by Sano di Pietro, 1 canvas fragment, 2 from the painting *Adoration of the Magi* by Bartolo di Fredi and 1 from the wooden frame, 2 from the painting *Madonna con Bambino* by Andrea di Niccolò, 1 from the painting *Natività* di Francesco di Giorgio Martini and 1 from the wall plaster.

Samples	Sampling points
1	Dentation of the stucco frame
2	Geometric frame
3	Vest of St. Augustine

Fig. 1. The wall painting "Majesty" (4.25 m × 2.15 m) by Ambrogio Lorenzetti (1335–1338), Piccolomini Chapel, St. Augustine Church (Siena, Italy), with the three fragments sampling points. Additional analyses were conducted on samples of dust from flaking of the wall painting, gathered on the wooden bench below the wall painting itself.

Table 1
Short description of samples 4–7 collected from the St. Augustine Church (Siena, Italy) and of samples 8–21 collected from the other locations in Siena (Italy).

	Samples	Description
collected from the St. Augustine	4	on the right of the *Majesty* painting
Church (Siena, Italy)	5	on the left of the *Majesty* painting
	6	floor dust nave
	7	floor dust of *Cappella Piccolomini*
collected from the other locations in Siena (Italy)	8–11	house dust Siena downtown
	12–14	Town center
	15	house dust Sienese country (*Pacina*)
	16	*Sano di Pietro* wooden table
	17	*Pinacoteca* canvas
	18, 19	paint fragment of *Adoration of the Magi* by *Bartolo di Fredi*
	20	wooden frame of *Adoration of the Magi* by *Bartolo di Fredi*
	21, 22	paint fragment of *Madonna con Bambino* by *Andrea di Niccolò*
	23	paint fragment of *Natività* by *Francesco di Giorgio Martini*
	24	*Pinacoteca* plaster

2.2. Fragments

The two fragments from the plaster frame of the "Majesty" by Ambrogio Lorenzetti, one from the wall paintings and the two fragments of the plaster from columns of the nave were scraped with a lancet and collected directly into an Eppendorf tube wrapped in aluminum foil. The same procedure was followed for the samples collected in Pinacoteca. The weight of the fragments ranged between 0.01 and 0.03 g.

2.3. Dust

Dust samples "dusting" of the wall painting were collected by a decontaminated spatula and placed in Eppendorf tubes wrapped in aluminum foil.

Floor dust samples for this study were obtained from vacuum cleaning bags. The vacuum cleaner was carefully cleaned between each sample. The bags were dismantled and the dust from individual bags was filtered through a 2 mm gage sieve onto a methanol and hexane rinsed aluminum foil to remove debris and other large particles. The sieve was cleaned and aluminum foil replaced between different samples. The samples were immediately transferred to methanol and hexane rinsed amber glass bottles and kept at 5 °C until analysis, that were performed on 2–3 g of dust.

3. Methodologies

3.1. Organic pollutants

Levels of contaminants (PAHs), chlorinated pesticides (4 isomers of hexachlorocyclohexane, hexachlorobenzene, isomers and metabolites of DDT and dieldrin), polychlorinated biphenyls (PCBs), 2 perfluoro alkylated compounds (PFOS and PFOA) and polybrominated diphenyl ethers (PBDEs), were determined by chromatography-mass spectrometry, after various steps of extraction and purification.

3.2. PFASs

PFOS and PFOA were extracted (from 2 samples of church's floor dust, 2 of wall painting dusting, 2 of wall painting frame and 1 from the sample of wooden table by Sano di Pietro) using an ion-pairing procedure and measured by using high performance liquid chromatography (HPLC) with electrospray ionization (ESI) tandem mass spectrometry. The analytical procedure for the extraction of samples followed a method widely tested (Governini et al., 2001; Corsolini et al., 2012; Guerranti et al., 2013a, 2013b). To avoid contamination and adsorption of the analytes during the sampling and extraction procedures, samples were never in contact with Teflon. Analytes separation was performed by using a Finnigan Surveyor Plus HPLC System equipped with a Betasil C18 column (50 × 2.1 mm i.d. and 5 μm particle size) supplied by Thermo Electron Corporation, San Jose, CA. Samples were injected in splitless mode.

Concentrations were evaluated in comparison to an unextracted standard curve of five points and, since we did not use an internal standard, data were not corrected for the recoveries. However, the reliability of the experimental protocols was checked by spiking and analyzing blank matrices (five samples of a similar wall dust were added with a 1 μL of a 50 ng/mL of PFOS/PFOA solution, with recoveries ranging from 89% to 95% for PFOS ad from 90% to 96% for PFOA). Chemicals and reagents were HPLC-grade and glassware was carefully washed to avoid sample crossover contamination. Blanks were analyzed with each set of five samples as a check for possible laboratory contamination and interferences; all the blanks resulted free from contamination. LOD, determined as three times the signal-to-noise (S/N) ratio, was 0.3 ng/g for PFOS and 0.4 ng/g for PFOA.

3.3. PAHs

Samples were extracted (Dionex mod. ASE 200 accelerated solvent extractor, Sunnyvale, USA) according to US-EPA (1996) method 3545A and quantified by high performance liquid chromatography (HPLC) equipped with a fluorimetric detector (FL) and a photodiode array detector (PDA) (Waters mod. 474 SFD and 996 PDA detectors, Milford, Massachusetts). All the samples collected have been analyzed for PAHs level. Samples were extracted by ASE with a mixture of dichloromethane/hexane at a temperature of 100 °C; the cells for the extraction have been packaged in the following way: filter, 5 g of alumina, filter, sample and diatomaceous earth. In cell was added the deuterated standard for recovery (phenanthrene-d 10). The extract was concentrated in a parallel evaporator at a temperature of about 40 °C, at a pressure of about 335 mbar. Subsequently, a purification was performed on chromatographic columns packed with florisil (2 g), by eluting the sample with 12 mL of hexane; samples were then evaporated in a rotavapor at a temperature of about 40 °C, at a pressure of about 335 mbar. The samples, extracted and purified, were concentrated under bland stream of nitrogen to a final volume of 50 μL. The chromatographic separation was performed on a Supelcosil™ LC-PAH HPLC chromatographic column (250 × 4.6 mm i.d., particle size 5 μm, Supelco) with an acetonitrile: water gradient of 60: 40 imposing a ramp to 100: 0 within 30 min and hold 10 min, with a

flow rate of 1.5 mL min. Quantitative analysis was done against a three-point linear calibration of PAH solution, obtained by dilution of the certified standard mixture TLC 16–PAH mix (Supelco). Satisfactory linearity was obtained, with values of the correlation coefficient R above 0.99. Detection limit, estimated as 3σ (IUPAC criterion) for each PAH compound was 0.1 ng/g. Procedural blanks and replicate samples were used as quality control procedures, and their reproducibility and recovery were high (>84%). The results presented are corrected on the basis of the internal standard recovery.

A confirmation of the results achieved by HPLC-FL/DAD was made using a GC/MS (ion trap detector) by Thermo-Finnigan (Trace™ GC 2000/Polaris) equipped with a Rtx-5MS capillary column (30 m × 0.25 mm, 0.25 mM) Restek. Samples were injected in split-less mode and helium was used as a carrier gas. The injector temperature was 250 °C, the temperature program of the oven was 100 °C (maintained for 2 min), increased by 10 °C/min up to 250 °C, then increased again by 0.8 °C/min up to 265 °C, and finally increased by 12 °C/min up to 325 °C (kept for 12 min). The spectrometer ran with EI^+ source (200 °C) with a temperature of transfer line equal to 280 °C and the energy of the filament equal to 70 eV. The data were acquired operating in single-ion monitoring mode. The quantitative results were in good agreement with HPLC analysis, but with higher limits of detection (between 0.5 ng/g to 0.9 ng/g). Therefore, data presented in the paper are those from HPLC analysis.

3.4. Chlorinated and brominated compounds

For PCBs, OCPs and PBDEs analysis, according to a method described by De Sanctis et al., 2013, samples (2 samples of church's floor dust, 2 of fresco dusting, 2 of fresco frame, 4 samples of floor dust from homes and the sample of wooden table by Sano di Pietro) were extracted using an accelerated solvent extractor (ASE, Dionex, Sunnyvale, USA, following US-EPA (1996) method 3545A) and identified and quantified by GC/MS (ion trap mass detector: Thermo-Finnigan, Trace™ GC 2000/GCQ Plus) with a RTX-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm particle size; Restek) using split-less injection mode and helium as carrier gas.

Analyses were performed on 20 BDE congeners commonly found in the environment (IUPAC numbers 3, 7, 15, 17, 23, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154 and 156), 12 OCPs/pesticide metabolites (hexachlorocyclohexanes: α-HCH, β-HCH, γ-HCH, δ-HCH; hexachlorobenzene: HCB; dieldrin; op' and pp' isomers of dichlorodiphenyldichloroethylene, dichlorodiphenyldichloroethane and dichlorodiphenyltrichloroethane: op'-DDE, pp'-DDE, op'-DDD, pp'-DDD, op'-DDT, pp'-DDT) and 52 PCB congeners (IUPAC numbers 8, 18, 28, 44, 52, 56, 60, 66, 101, 105, 110, 114, 118, 123, 128, 134, 135, 137, 138, 141, 144, 146, 149, 151, 153, 156, 157, 158, 167, 170, 171, 172, 174, 176, 177, 178, 180, 183, 185, 187, 189, 194, 195, 196, 199, 201, 202, 205, 206, 207 and 209).

Detection limits, calculated as the mean blank 3σ, were 4 pg/g for PBDE congeners and 0.01 ng/g for PCB congeners and pesticides.

3.5. VOCs

The VOCs analyzed were BTEX (benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene); compounds collected on sorbing cartridges were desorbed directly into the glass storage tube for about 30 min by using 2 mL of carbondisulfide (CS_2, low benzene, Sigma Aldrich) and 10 μL of internal standard solution, prior to analysis. Standard solution was made by dissolving 10 mg of *o*-dichlorobenzene (Sigma) in 10 mL of CS_2. In parallel, the same determination was conducted with a recently developed method, by using CH_2Cl_2 in an appositely devised soxhlet apparatus (Cucciniello et al., 2015) and results were found to be consistent between the two methods. The relative standard deviation was lower than 4% in all cases. Analyses were done by GC-FID (Agilent 7890A) equipped with HP-5 column (60 m × 0.2 mm id). GC oven was programmed for 60 °C hold for 2 min and ramped to 140 °C at a rate of 6 °C with 2 min hold at 140 °C and ramped to 250 °C at a rate of 20 °C/min with 10 min hold at 250 °C. Helium was used as carrier gas with flow rate of 1 mL/min and split ratio 1:10.

Air pollution was assessed by placing five passive samplers for 31 days both inside and outside the church. The sampling period was chosen to capture a representative amount of BTEX compounds for the analyses without reaching the saturation of the sorbent material (Gorecki and Namiesnik, 2002; Seethapathy et al., 2008).

The samplers placed inside the church were identified by the letter "I" and were located as follows:

I1: under the wall painting "Majesty", in the Piccolomini Chappel
I2: in the middle room, on the base of a column, in the Piccolomini Chappel
I3: under the altar of Sodoma, in the Piccolomini Chappel
I4: above the base of a column near the altar in the central nave
I5: above the base of a column near the main door

The samplers placed outdoor were identified by the letter "E" and were located as follows:

E1: Via S. Quirico
E2: Via Campansi
E3: Via delle Cerchia
E4: Botanical Garden (in the garden)
E5: Via delle Sperandie
E6: Botanical Garden (close to road)
E7: Via delle Sperandie (in a private garden)

All sampling points are located in "controlled traffic" areas inside the city walls of Siena. Botanical Garden (E4) and the private garden in Via delle Sperandie (E7), are no-cars areas.

The passive sampler, RING (Aquaria Research srl), consists of an adsorbent cartridge packed with 300 mg of activated coconut charcoal inserted in a microporous polyethylene membrane. The compounds diffuse through the membrane towards the cartridge driven by the gradient of concentration between the ambient air and the inner cartridge. Compound concentrations C (mg/m^3) can be calculated by applying an equation derived from Fick's first law of diffusion (Cussler, 2009; Rossi et al., 2015):

$$C = \frac{m_d - m_b}{P \times t \times 10^{-6}}$$

Where m_d is the adsorbed mass in mg of the analyte sampled during the time t (min) while m_b is the mass of the analyte on a non-exposed cartridge (blank), P (mL/min) is the diffusive uptake rate of the substances (73 mL/min for benzene, 66 mL/min for toluene, 60 mL/min for ethylbenzene, 58 mL/min for o-xylene and 64 mL/min for m&p-xylenes); P values were supplied by the RING manufacturer and were adjusted for temperature using a multiplying factor $\left(\frac{298}{273 + T}\right)^{1.5}$ where T was expressed in Celsius degrees.

Samplers were exposed at a height of approximately 4 m above the street level, outside and 1 m above the floor level, inside the church. After the sampling, all the exposed cartridges were stored at less than 4 °C and analyzed within a week.

4. Results and discussion

The compounds detected by the analysis carried out were limited in number and they belonged only to the classes of PAHs and PBDEs; all other classes of compounds were found to be lower than the relative LODs (data not shown). Table 2 reports the concentrations of the chemical compounds present in the samples collected from the Church of St. Augustine. The prevalence of the most volatile compounds among the classes of PBDEs and PAHs was observed in almost all the samples analyzed. Most of PAHs consisted of 3–4 aromatic rings (phenanthrene, anthracene, fluoranthene; Σ16PAH range: 1.18–60.68 ng/g). The Phe/Ant ratio was found to be < 10 in all cases; this suggests a pyrolytic origin of these pollutants, associated with combustion phenomena and emissions from vehicular traffic (Sicre et al., 1987; Budzinski et al., 1997). An exception to these results was represented by a wall painting fragment, collected from the black color area painted with black carbon pigment (Damiani et al., 2014), in which 13 of the 15 analyzed PAHs were detected, in concentrations considerably higher than those of all other samples analyzed. The results obtained also showed a gradient of contamination that follows the order 'floor powder' > 'fresco dusting' > 'frame'; this suggests a transfer of organic compounds from the surface of the fresco followed by an accumulation in the surrounding environment (Damiani et al., 2014).

10 out of the 20 PBDE congeners analyzed were detected in the samples. Prevailing congeners were: BDE-47 that is among the most commonly encountered in environment and animals, being present in many materials and products (Renner, 2000), BDE 126 and BDE 77 at lower concentrations.

The analysis showed no detectable traces of any of the 51 PCB congeners analyzed, chlorinated pesticides and PFASs.

The Church is set in the urban context of Siena, within the walls of the city where, due to the lack of industrial activity, the main source of atmospheric contamination is represented by vehicular traffic, to which, in the winter months, the domestic heating is added.

By a review carried out within the scientific literature, it appeared that analyses of the contaminants considered in this study were never made previously in fragments of art works. Instead, it was possible to find data in the literature referring to the presence of PAHs in stone dust and stone black crust sampled from the external surfaces of monuments (Gianguzza et al., 2004; Martínez-Arkarazo et al., 2007; Orecchio, 2010). Therefore, in the present study, samples collected from the different settings (Table 3) were analyzed to compare the levels of contaminants with those detected from samples collected in the Church of St. Augustine (Table 2).

The levels of pollutants and the pattern in the samples from the Pinacoteca were comparable with those collected in the church of St. Augustine, both for PAHs (except black color fragment, for which it is assumed the presence of coal) and for PBDEs. The levels of PAHs detected in this work were found generally lower respect to those reported in the literature for other Italian towns. Orecchio (2010) reported an average level of PAHs of 40 ng/g, ranging in the interval 18–84 ng/g, in stones samples from the Temples of Agrigento (Italy); also, the PAHs concentrations observed in this study were much lower than those reported for the sum of 19 PAHs in Palermo stone monuments (77–9798 ng/g) (Gianguzza et al., 2004).

This is due to the fact that the samples from Palermo and from the Temples of Agrigento comes from outdoors materials, and thus more exposed to vehicular and industrial pollution. Moreover, Palermo is more populated than Siena and, additionally, the monuments studied in Palermo are located in very narrow streets where the dilution of pollutants is limited and PAHs and other substances remain in contact with the stone for longer time (Orecchio, 2010).

Table 2
Concentrations (ng/g) of the PAHs and PBDEs compounds, detected in samples collected from the Church of Saint Augustine (Siena, Italy). Compounds not reported here were below the LODs in all samples and all the samples not reported here resulted with levels < LODs for all compounds.

		Majesty dusting right	*Majesty* dusting left	*Majesty* Dentation of the stucco frame (*Sample 1*)	*Majesty* Geometric frame (*Sample 2*)	Floor dust nave	Cappella Piccolomini floor dust	*Majesty* black fragment
PAHs	Naph	<LOD	<LOD	<LOD	<LOD	60.68	53.2	<LOD
	Acy	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	140300.55
	Ace	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	70327.87
	Fln	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	9706.75
	Phe	1.23	1.31	1.02	1.03	<LOD	<LOD	2269.74
	Ant	1.43	<LOD	<LOD	<LOD	<LOD	<LOD	4435.59
	Flt	1.02	<LOD	<LOD	<LOD	<LOD	<LOD	2465.26
	Pyr	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2801.28
	BaA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1191.45
	Chr	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1715.36
	BbF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1256.90
	BkF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2018.72
	BaP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	982.04
	DBahA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	1725.16
	BghiP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	∑PAHs	3.68	1.31	1.02	1.03	60.68	53.20	241196.68
PBDEs	17	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	49	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	71	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	47	0.45	0.49	<LOD	<LOD	4.29	10.89	–
	66	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	77	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	99	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	85	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	–
	126	0.35	0.37	<LOD	<LOD	<LOD	<LOD	–
	∑PBDEs	0.80	0.86	<LOD	<LOD	4.29	10.89	–

Table 3
Concentrations (ng/g) of the PAHs and PBDEs compounds, detected in samples collected in different settings. Compounds not reported here were below the LODs in all samples and all samples not reported here resulted with levels < LODs for all compounds.

		Samples							
		House dust Siena downtown (*Sample 1*)	House dust Siena downtown (*Sample 2*)	House dust Siena downtown (*Sample 3*)	House dust sienese country (Pacina) (*Sample 4*)	Sano di Pietro Wooden table	Pinacoteca canvas	Pinacoteca plaster	Bartolo di Fredi *Adoration of the Magi* Painting fragment
PAHs	Naph	834.38	1625.36	606.49	20.44	<LOD	<LOD	<LOD	1.682
	Acy	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Ace	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Fln	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Phe	491.74	1000.65	243.51	10.65	1.59	3.80	0.14	<LOD
	Ant	199.34	206.37	115.43	1.43	<LOD	8.82	1.04	<LOD
	Flt	175.398	173.841	36.498	9.493	<LOD	7.16	<LOD	<LOD
	Pyr	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	BaA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Chr	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	BbF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	BkF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	BaP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	DBahA	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	BghiP	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	∑PAHs	1700.85	3006.23	1002.02	42.00	1.59	19.77	1.179	1.68
PBDEs	17	<LOD	3.29	<LOD	<LOD	<LOD	–	–	–
	28	<LOD	12.58	22.59	<LOD	<LOD	–	–	–
	49	<LOD	28.40	13.59	4.73	<LOD	–	–	–
	71	<LOD	30.54	18.39	4.53	<LOD	–	–	–
	47	47.294	495.98	482.59	87.59	0.91	–	–	–
	66	<LOD	10.53	12.57	<LOD	<LOD	–	–	–
	77	20.569	42.69	15.393	5.184	0.54	–	–	–
	99	<LOD	4.29	<LOD	<LOD	<LOD	–	–	–
	85	<LOD	2.483	<LOD	<LOD	<LOD	–	–	–
	126	16.32	52.59	43.28	3.17	0.98	–	–	–
	∑PBDEs	84.19	683.37	608.42	105.21	2.43	–	–	–

The floor dust levels of PBDEs and PAHs were lower in the Church of St. Augustine compared to the houses of the city center and of the countryside. Very different patterns of contaminants were found: only naphthalene and BDE-47 were found in the church dust samples. PBDEs levels in the dust samples from the church were about 7–140 times lower than those of the dust picked up in homes in the center of Siena and about 9–21 times lower than the dust picked up in the house in the countryside. While, concerning PAHs, the levels in the dust samples from the church were about 16–56 times lower than those in the dust picked up in homes in the center of Siena but higher than those of the dust from the house in the countryside. This fact can be attributed to the scarce traffic in the countryside respect to the traffic in town, a factor that greatly affects the air and dust contamination. The difference in the levels of PAHs and PBDEs in samples taken in the Church and in the town houses, together with the fact that only the most volatile among the 15 PAHs analyzed was present in the dust of the church, demonstrated the effectiveness of the closure to the public as a form of preservation of cultural heritage from the effects of air pollution. From the many studies in the scientific literature (Chen et al., 2014; Kefeni et al., 2014; Krol et al., 2014; Lim et al., 2014; Qi et al., 2014; Hassan and Shoeib, 2015; Lankova et al., 2015; Zhu et al., 2015; just to mention the most recent) it is evident, both for PBDEs and PAHs, an extreme variability in the levels of these compounds in the dust of various indoor environments, with values ranging from <0.3 ng/g (Kefeni et al., 2014) to 45140 ng/g (Lim et al., 2014) and from 0.036 μg/g (Mannino and Orecchio, 2008) to 466 μg/g (Qi et al., 2014) for ∑PBDEs and ∑PAHs, respectively.

In Table 4 the results of BTEX analysis are reported as averaged values of 3 determinations for each point. In most cases the values detected inside the church are below LOD (limit of detection) and always below the limit imposed by the Italian law for such a kind of environment (Legislative Decree, no 152, 2006). Only with respect to Toluene in the indoor measurements we could observe a slightly

Table 4
Air BTEX concentration ($\mu g/m^3$).

Samples	Benzene ($\mu g/m^3$) LOD = 0.01 $\mu g/m^3$	Toluene ($\mu g/m^3$) LOD = 0.05 $\mu g/m^3$	Ethylbenzene ($\mu g/m^3$) LOD = 0.01 $\mu g/m^3$	Xylenes ($\mu g/m^3$) LOD = 0.01 $\mu g/m^3$
I1	0.02	0.76	<LOD	<LOD
I2	0.01	<LOD	<LOD	<LOD
I3	<LOD	0.29	<LOD	<LOD
I4	0.05	0.3	0.35	0.35
I5	0.02	1.4	0.22	<LOD
E1	0.04	1.66	0.3	0.13
E2	0.03	4.91	0.95	0.52
E3	0.15	0.68	0.12	0.55
E4	0.18	2.36	0.04	0.10
E5	0.24	2.07	0.5	0.68
E6	0.19	0.86	0.14	0.22
E7	0.04	0.37	0.04	0.10

higher value, specifically in the sampling point located to the church entrance facing the street. This value could be associated with the presence of toluene in the outside street, probably due to the vehicular traffic. In fact, in Table 4, we could observe higher values in the outdoors sampling point, though always below the acceptable limit.

5. Conclusions

A monitoring campaign of some organic pollutants was conducted on the "Majesty" wall painting by Ambrogio Lorenzetti in the Church of St. Augustine and on some paintings in Pinacoteca Nazionale of Siena (Siena, Italy) together the air quality evaluation of the Siena downtown. The results showed low levels of some organic pollutants, such as PAHs and PBDEs. In addition, the levels of PAHs and PBDEs of the dust samples of the Church of St. Augustine were lower than those collected from the houses in the downtown of Siena and in the countryside. These results indicated that the indoor environment of the church presented a high-quality condition and, as a consequence, it was well-suited to the protection of its paintings.

Conflict of interest

The authors declare no conflict of interest.

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