ANNEX 1 - DIFFRACTION DATA

ANNEX 1 – DIFFRACTION DATA

	Angle (°)	d value (Å)	Intensity (Count)	Intensity (%)
d=4.94097	17.938	4.94097	119	0.5
d=3.83163	23.195	3.83163	762	3
d=3.29970	27.000	3.29970	73	0.3
d=3.15123	28.298	3.15123	367	1.4
d=3.01928	29.562	3.01928	25486	100
d=2.87682	31.062	2.87682	1578	6.2
d=2.82818	31.610	2.82818	375	1.5
d=2.66019	33.664	2.66019	86	0.3
d=2.53086	35.440	2.53086	63	0.2
d=2.48355	36.138	2.48355	1098	4.3
d=2.39820	37.471	2.39820	69	0.3
d=2.37408	37.866	2.37408	61	0.2
d=2.27493	39.584	2.27493	1744	6.8
d=2.18686	41.249	2.18686	193	0.8
d=2.08647	43.331	2.08647	1402	5.5
d=2.01102	45.044	2.01102	92	0.4
d=1.98751	45.607	1.98751	75	0.3
d=1.94958	46.546	1.94958	70	0.3
d=1.91980	47.311	1.91980	584	2.3
d=1.90418	47.723	1.90418	1900	7.5
d=1.86807	48.705	1.86807	1625	6.4
d=1.80083	50.649	1.80083	148	0.6
d=1.78305	51.191	1.78305	138	0.5
d=1.66717	55.038	1.66717	44	0.2
d=1.62052	56.763	1.62052	235	0.9
d=1.59908	57.595	1.59908	638	2.5
d=1.58099	58.317	1.58099	136	0.5

Table A1.1 Diffractometric data of Carrara Marble sample.

	Angle (°)	d value (Å)	Intensity (Count)	Intensity (%)
d=3.84921	23.088	3.84921	1008	10
d=3.46580	25.683	3.46580	63	0.6
d=3.32104	26.823	3.32104	82	0.8
d=3.16197	28.200	3.16197	171	1.7
d=3.03115	29.444	3.03115	10091	100
d=2.89866	30.822	2.89866	109	1.1
d=2.83769	31.502	2.83769	310	3.1
d=2.59853	34.487	2.59853	66	0.7
d=2.49039	36.035	2.49039	1237	12.3
d=2.28145	39.466	2.28145	1655	16.4
d=2.09109	43.230	2.09109	1390	13.8
d=1.92451	47.189	1.92451	536	5.3
d=1.90969	47.577	1.90969	1424	14.1
d=1.87300	48.569	1.87300	1581	15.7
d=1.62389	56.635	1.62389	297	2.9
d=1.60232	57.467	1.60232	613	6.1
d=1.58312	58.231	1.58312	95	0.9

Table A1.2 Diffractometric data of NBE1 sample.

ANNEX 1 – DIFFRACTION DATA

	Angle (°)	d value (Å)	Intensity (Count)	Intensity (%)
d=3.84705	23.101	3.84705	945	8.4
d=3.70497	24.000	3.70497	102	0.9
d=3.31661	26.860	3.31661	95	0.8
d=3.22865	27.606	3.22865	76	0.7
d=3.16206	28.199	3.16206	191	1.7
d=3.02875	29.468	3.02875	11204	100
d=2.89751	30.835	2.89751	1570	14
d=2.83700	31.509	2.83700	307	2.7
d=2.68232	33.378	2.68232	66	0.6
d=2.48982	36.044	2.48982	1210	10.8
d=2.40919	37.294	2.40919	82	0.7
d=2.38066	37.757	2.38066	74	0.7
d=2.28035	39.486	2.28035	1587	14.2
d=2.19874	41.016	2.19874	170	1.5
d=2.09039	43.246	2.09039	1435	12.8
d=2.02038	44.824	2.02038	109	1
d=1.92358	47.213	1.92358	529	4.7
d=1.90912	47.592	1.90912	1347	12
d=1.87198	48.597	1.87198	1508	13.5
d=1.81489	50.229	1.81489	127	1.1
d=1.79464	50.836	1.79464	118	1.1
d=1.62380	56.638	1.62380	272	2.4
d=1.60196	57.482	1.60196	656	5.9
d=1.58388	58.200	1.58388	100	0.9

Table A1.3 Diffractometric data of NBE2 sample.

ANNEX 2 – COLORIMETRIC DATA

ANNEX 2 – COLORIMETRIC DATA

EXP. TIME	ORIENTATION	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
6 M	H	84.50 ± 1.10	-0.04 ± 0.04	2.48 ± 0.23	-5.09 ± 1.10	0.42 ± 0.04	2.34 ± 0.23	5.65 ± 0.93
12 M	H	83.91 ± 1.42	0.16 ± 0.15	4.16 ± 0.78	-5.69 ± 1.42	0.62 ± 0.15	4.02 ± 0.78	7.00 ± 1.59
	O	83.65 ± 1.72	0.19 ± 0.20	3.92 ± 0.70	-5.95 ± 1.72	0.65 ± 0.20	3.78 ± 0.70	7.09 ± 1.80
	V	89.40 ± 0.91	-0.34 ± 0.03	0.22 ± 0.05	-0.20 ± 0.91	0.12 ± 0.03	0.08 ± 0.05	0.67 ± 0.58
18 M	H	85.78 ± 1.18	-0.02 ± 0.06	2.45 ± 0.38	-3.82 ± 1.18	0.44 ± 0.06	2.31 ± 0.38	4.51 ± 1.14
	O	85.32 ± 1.15	0.24 ± 0.03	2.86 ± 0.14	-4.27 ± 1.15	0.70 ± 0.03	2.73 ± 0.14	5.16 ± 0.91
	V	86.94 ± 3.16	-0.30 ± 0.04	0.07 ± 0.11	-2.66 ± 3.16	0.15 ± 0.04	-0.07 ± 0.11	2.67 ± 3.16
24 M	H	83.43 ± 4.66	0.29 ± 0.32	4.84 ± 1.92	-6.17 ± 4.66	0.74 ± 0.32	4.70 ± 1.92	7.90 ± 4.85
	O	82.17 ± 2.10	0.23 ± 0.09	4.44 ± 0.70	-7.43 ± 2.10	0.69 ± 0.09	4.30 ± 0.70	8.63 ± 2.11
	V	89.93 ± 0.17	-0.27 ± 0.01	0.72 ± 0.12	0.33 ± 0.17	0.19 ± 0.01	0.58 ± 0.12	0.71 ± 0.11

Table A2.1 Mean colorimetric data (L*, a*, b*) and colour variations (ΔL*, Δa*, Δb* and ΔE*) of Carrara Marble samples calculated between data acquired before and after 6, 12, 18 and 24 months of exposure in Bologna. H, O, V stand for specimens horizontally, obliquely and vertically placed.

EXP. TIME	ORIENTATION	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
6 M	H	79.87 ± 1.37	0.19 ± 0.09	4.96 ± 0.53	-9.73 ± 1.37	0.65 ± 0.09	4.82 ± 0.53	10.88 ± 1.39
12 M	H	77.52 ± 1.94	0.48 ± 0.08	6.31 ± 0.50	-12.07 ± 1.94	0.94 ± 0.08	6.17 ± 0.50	13.60 ± 1.87
	O	88.02 ± 1.42	-0.08 ± 0.02	1.79 ± 0.43	-1.57 ± 1.42	0.38 ± 0.02	1.65 ± 0.43	2.44 ± 1.21
	V	90.85 ± 0.32	-0.31 ± 0.02	0.22 ± 0.16	1.26 ± 0.32	0.15 ± 0.02	0.08 ± 0.16	1.28 ± 0.31
18 M	H	71.97 ± 3.22	0.80 ± 0.09	7.98 ± 0.49	-17.63 ± 3.22	1.25 ± 0.09	7.84 ± 0.49	19.35 ± 3.11
	O	78.89 ± 0.95	0.52 ± 0.05	6.29 ± 0.16	-10.71 ± 0.95	0.98 ± 0.05	6.15 ± 0.16	12.39 ± 0.89
	V	90.07 ± 1.18	-0.33 ± 0.06	0.57 ± 0.38	0.47 ± 1.18	0.12 ± 0.06	0.44 ± 0.38	1.26 ± 0.32
24 M	H	71.03 ± 1.53	1.10 ± 0.09	9.33 ± 0.28	-18.57 ± 1.53	1.55 ± 0.09	9.19 ± 0.28	20.78 ± 1.46
	O	76.28 ± 2.75	0.80 ± 0.11	7.46 ± 0.37	-13.32 ± 2.75	1.26 ± 0.11	7.32 ± 0.37	15.28 ± 2.59
	V	90.32 ± 0.52	-0.30 ± 0.05	0.77 ± 0.16	0.72 ± 0.52	0.16 ± 0.05	0.63± 0.16	1.05 ± 0.33

Table A2.2 Mean colorimetric data (L*, a*, b*) and colour variations (ΔL*, Δa*, Δb* and ΔE*) of Carrara Marble samples calculated between data acquired before and after 6, 12, 18 and 24 months of exposure in Ferrara. H, O, V stand for specimens horizontally, obliquely and vertically placed.

EXP. TIME	ORIENTATION	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
6 M	H	63.64 ± 0.95	6.69 ± 1.05	15.04 ± 0.58	-3.65 ± 0.95	-0.58 ± 1.05	-1.61 ± 0.58	4.20 ± 0.79
12 M	H	65.82 ± 1.97	6.16 ± 0.87	14.95 ± 0.59	-1.48 ± 1.97	-1.11 ± 0.87	-1.70 ± 0.59	2.91 ± 1.51
	O	68.07 ± 2.26	6.18 ± 1.15	14.13 ± 0.25	0.78 ± 2.26	-1.09 ± 1.15	-2.52 ± 0.25	3.53 ± 1.06
	V	69.68 ± 2.12	6.48 ± 1.36	15.33 ± 0.29	2.39 ± 2.12	-0.80 ± 1.36	-1.32 ± 0.29	3.41 ± 1.41
18 M	H	60.29 ± 0.70	5.00 ± 0.58	14.27 ± 0.28	-7.00 ± 0.70	-2.27 ± 0.58	-2.38 ± 0.28	7.74 ± 0.81
	O	64.49 ± 1.13	6.54 ± 0.36	18.86 ± 1.04	-2.80 ± 1.13	-0.73 ± 0.36	2.21 ± 1.04	3.75 ± 1.22
	V	68.78 ± 1.88	6.55 ± 0.72	14.66 ± 1.20	1.48 ± 1.88	-0.72 ± 0.72	-1.99 ± 1.20	3.20 ± 1.02
24 M	H	60.53 ± 1.33	4.91 ± 0.66	14.18 ± 0.53	-6.76 ± 1.33	-2.37 ± 0.66	-2.47 ± 0.53	7.62 ± 1.29
	O	63.70 ± 1.80	5.98 ± 0.76	16.90 ± 1.81	-3.59 ± 1.80	-1.29 ± 0.76	0.25 ± 1.81	4.38 ± 1.19
	V	69.66 ± 1.37	6.42 ± 0.80	13.54 ± 0.67	2.37 ± 1.37	-0.86 ± 0.80	-3.11 ± 0.67	4.19 ± 1.05

Table A2.3 Mean colorimetric data (L*, a*, b*) and colour variations (ΔL*, Δa*, Δb* and ΔE*) of Verona Red Marble samples calculated between data acquired before and after 6, 12, 18 and 24 months of exposure in Ferrara. H, O, V stand for specimens horizontally, obliquely and vertically placed.

EXP. TIME	ORIENTATION	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
6 M	H	76.13 ± 1.52	0.25 ± 0.10	3.75 ± 0.51	-13.47 ± 1.52	0.70 ± 0.10	3.62 ± 0.51	13.97 ± 1.60
12 M	H	74.53 ± 1.33	0.37 ± 0.03	5.10 ± 0.40	-15.06 ± 1.33	0.83 ± 0.03	4.96 ± 0.40	15.88 ± 1.39
	O	76.92 ± 2.22	0.38 ± 0.16	3.85 ± 0.85	-12.68 ± 2.22	0.84 ± 0.16	3.71 ± 0.85	13.24 ± 2.37
	V	87.96 ± 0.66	-0.15 ± 0.06	-0.05 ± 0.06	-1.64 ± 0.66	0.30 ± 0.06	-0.19 ± 0.06	1.68 ± 0.65
18 M	H	61.91 ± 1.82	1.07 ± 0.10	7.13 ± 0.28	-27.68 ± 1.82	1.53 ± 0.10	6.99 ± 0.28	28.59 ± 1.83
	O	69.41 ± 2.15	0.71 ± 0.27	5.39 ± 0.81	-20.18 ± 2.15	1.17 ± 0.27	5.25 ± 0.81	20.89 ± 2.29
	V	88.13 ± 0.69	-0.20 ± 0.17	0.13 ± 0.34	-1.47± 0.69	0.25 ± 0.17	0.00 ± 0.34	1.54 ± 0.64
24 M	H	59.64 ± 1.92	1.35± 0.10	8.63 ± 0.37	-29.96 ± 1.92	1.80 ± 0.10	8.49 ± 0.37	31.19 ± 1.95
	O	64.72 ± 1.37	1.20 ± 0.05	7.67 ± 0.24	-24.88 ± 1.37	1.66 ± 0.05	7.53 ± 0.24	26.05 ± 1.36
	V	88.2 8 ± 0.64	-0.28 ± 0.17	0.09 ± 0.17	-1.31 ± 0.64	0.18 ± 0.17	-0.04 ± 0.17	1.36 ± 0.61

Table A2.4 Mean colorimetric data (L*, a*, b*) and colour variations (ΔL*, Δa*, Δb* and ΔE*) of Carrara Marble samples calculated between data acquired before and after 6, 12, 18 and 24 months of exposure in Ferrara. H, O, V stand for specimens horizontally, obliquely and vertically placed.

ANNEX 3 – WATER-SOLUBLE DATA OF STONE DEPOSIT

ANNEX 3 – WATER-SOLUBLE DATA OF STONE DEPOSIT

EXP. TIME	SAMPLE	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)
6 M	BCH11	36.00	15.34	5.92	24.72	0.44	1.06	7.00	12.18
12 M	BCH13	26.35	15.35	8.05	22.86	<LOD	1.75	5.08	<LOD
	BCO3	21.35	14.82	8.67	20.36	0.22	1.53	6.22	4.88
18 M	BCH7	30.90	<LOD	4.43	21.78	<LOD	0.55	5.94	18.24
	BCO11	27.93	<LOD	6.25	19.59	<LOD	0.65	5.61	16.06
24 M	BCH6	0.97	2.10	2.68	0.62	0.01	0.07	0.18	5.87
	BCO12	1.68	2.00	4.22	1.03	<LOD	0.23	0.20	4.77
	BCV2	0.12	0.26	0.41	0.06	0.01	0.01	0.03	0.77

Table A3.1 Concentration of soluble ions measured in material deposited on Carrara Marble samples exposed in Bologna for 6, 12, 18 and 24 months. <LOD means below the limit of detection.

EXP. TIME	SAMPLE	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)
6 M	PTCH22	29.82	12.59	7.00	20.28	0.14	1.42	5.86	15.39
12 M	PTCH18	17.29	15.98	12.38	16.46	<LOD	1.92	5.14	<LOD
	PTCO11	17.60	13.12	9.31	17.44	<LOD	1.55	6.02	9.06
18 M	PTCH12	31.64	13.21	18.98	23.77	2.55	3.92	6.52	17.01
	PTCO6	28.04	12.13	23.66	22.46	0.09	1.63	6.66	17.04
24 M	PTCH13	6.28	4.33	6.31	3.37	0.17	1.89	0.55	11.43
	PTCO7	4.41	5.44	20.08	2.48	0.46	0.81	0.93	21.37
	PTCO20 *	0.73	1.59	3.04	0.38	0.05	0.14	0.20	3.79
	PTCV2	0.87	1.25	7.36	0.46	<LOD	0.13	0.13	3.98

*Table A3.2 Concentration of soluble ions measured in material deposited on Carrara Marble samples exposed in Ferrara for 6, 12, 18 and 24 months. <LOD means below the limit of detection. * refers to specimen obliquely placed on window balcony.*

EXP. TIME	SAMPLE	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)
6 M	PTNH22	27.70	11.08	2.95	19.56	0.05	1.00	5.11	10.53
12 M	PTNH19	22.24	17.04	6.53	21.80	0.27	1.68	6.34	<LOD
	PTNO11	19.61	13.30	4.76	18.96	0.01	1.47	6.61	7.24
18 M	PTNH12	45.05	8.96	3.78	19.74	1.08	20.09	5.71	20.83
	PTNO15	21.32	6.61	2.23	17.47	1.02	1.00	5.18	14.23
24 M	PTNH13	1.54	2.43	3.11	1.10	<LOD	0.44	0.42	11.07
	PTNO17	0.99	1.93	1.77	0.75	0.30	0.13	0.27	6.48
	PTNO20 *	0.45	1.21	1.47	0.24	0.12	0.12	0.09	3.46
	PTNV3	0.30	0.37	8.13	0.20	<LOD	0.08	0.07	4.71

*Table A3.3 Concentration of soluble ions measured in material deposited on Verona Red Marble samples exposed in Ferrara for 6, 12, 18 and 24 months. <LOD means below the limit of detection. * refers to specimen obliquely placed on window balcony.*

EXP. TIME	SAMPLE	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Na^+ (ppm)	NH_4^+ (ppm)	K^+ (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)
6 M	SMCH2	35.87	15.71	9.30	24.87	0.67	1.51	7.82	20.34
	SMCO2	28.90	11.49	8.19	19.47	<LOD	1.25	5.72	16.06
12 M	SMCH3	14.78	6.36	5.71	11.81	<LOD	0.58	0.49	<LOD
	SMCO3	32.33	13.99	14.65	29.48	<LOD	2.62	5.88	<LOD
18 M	SMCH6	36.32	10.18	13.57	25.78	0.36	1.54	6.47	19.33
	SMCO6	35.97	9.81	12.31	25.97	0.41	1.45	7.27	24.37
24 M	SMCH7	6.04	4.26	13.82	3.23	0.23	0.41	0.38	15.92
	SMCO7	5.37	4.27	15.98	3.31	0.03	0.83	0.53	22.84
	SMCV3	0.83	2.44	8.73	0.49	<LOD	0.35	0.09	6.34

Table A3.4 Concentration of soluble ions measured in material deposited on Carrara Marble samples exposed in Bologna for 6, 12, 18 and 24 months. <LOD means below the limit of detection.

ANNEX 4 – CARBON FRACTIONS OF STONE DEPOSIT

EXP. TIME	SAMPLE	TC (wt%)	CC (wt%)	OC (wt%)	EC (wt%)
6 M	BCH10	14.70	6.15	7.38	1.17
12 M	BCH12	16.61	6.03	7.54	3.03
	BCO2	15.93	5.43	9.83	0.67
18 M	BCH8	14.64	7.08	5.74	1.82
	BCO10	14.25	5.82	7.57	0.85
24 M	BCH14	12.73	6.58	n.d.	n.d.
	BCO5	21.10	3.99	10.25	6.86

Table A4.1 Concentration of carbon fractions measured in material deposited on Carrara Marble samples exposed in Bologna for 6, 12, 18 and 24 months. N.d.. stands for not detected.

EXP. TIME	SAMPLE	TC (wt%)	CC (wt%)	OC (wt%)	EC (wt%)
6 M	PTCH21	15.62	3.22	11.24	1.16
12 M	PTCH23	16.91	4.63	9.10	3.18
	PTCO12	16.56	3.91	11.37	1.27
18 M	PTCH4	14.11	3.10	8.11	2.90
	PTCO5	14.22	2.37	9.34	2.51
24 M	PTCH5	15.51	1.80	7.0	6.72
	PTCO4	13.68	2.06	7.67	3.96

Table A4.2 Concentration of carbon fractions measured in material deposited on Carrara Marble samples exposed in Ferrara for 6, 12, 18 and 24 months.

EXP. TIME	SAMPLE	TC (wt%)	CC (wt%)	OC (wt%)	EC (wt%)
6 M	PTNH21	16.86	3.37	n.d.	n.d.
12 M	PTNH17	17.16	2.79	9.26	5.11
	PTNO12	18.97	2.69	14.30	1.98
18 M	PTNH4	13.90	2.75	11.38	0.00
	PTNO14	14.87	3.13	11.42	0.32
24 M	PTNH11	13.40	2.08	8.00	3.32
	PTNOI6	17.75	2.15	11.16	4.43

Table A4.3 Concentration of carbon fractions measured in material deposited on Verona Red Marble samples exposed in Ferrara for 6, 12, 18 and 24 months.

EXP. TIME	SAMPLE	TC (wt%)	CC (wt%)	OC (wt%)	EC (wt%)
6 M	SMCH1	12.34	4.51	6.67	1.16
	SMCO1	11.72	5.63	5.02	1.07
12 M	SMCH4	14.50	2.73	8.50	3.27
	SMCO4	13.61	3.22	8.01	2.38
18 M	SMCH5	9.91	4.00	4.95	0.96
	SMCO5	9.82	4.38	5.18	0.26
24 M	SMCH8	8.95	3.86	3.10	1.99
	SMCO8	8.86	3.43	3.00	2.43

Table A4.4 Concentration of carbon fractions measured in material deposited on Carrara Marble samples exposed in Florence for 6, 12, 18 and 24 months.

ANNEX 5 – WATER-SOLUBLE DATA OF PASSIVE FILTERS

EXP. TIME	SAMPLE	Cl^- ($\mu g\ cm^{-2}$)	NO_3^- ($\mu g\ cm^{-2}$)	SO_4^{2-} ($\mu g\ cm^{-2}$)	Na^+ ($\mu g\ cm^{-2}$)	NH_4^+ ($\mu g\ cm^{-2}$)	K^+ ($\mu g\ cm^{-2}$)	Mg^{2+} ($\mu g\ cm^{-2}$)	Ca^{2+} ($\mu g\ cm^{-2}$)
6 M	PC84	34.41	1.93	14.03	17.79	0.88	2.18	2.37	38.95
12 M	PC85	7.49	23.17	8.14	7.03	<LOD	5.43	1.39	65.30
18 M	PC86	64.40	32.10	4.25	2.74	0.41	1.57	<LOD	47.14
24 M	PC87	17.53	8.19	3.81	2.79	0.71	3.09	0.93	37.11

Table A5.1 Concentration of soluble ions measured in passive filters exposed in Bologna for 6, 12, 18 and 24 months. <LOD means below limit of detection.

EXP. TIME	SAMPLE	Cl^- ($\mu g\ cm^{-2}$)	NO_3^- ($\mu g\ cm^{-2}$)	SO_4^{2-} ($\mu g\ cm^{-2}$)	Na^+ ($\mu g\ cm^{-2}$)	NH_4^+ ($\mu g\ cm^{-2}$)	K^+ ($\mu g\ cm^{-2}$)	Mg^{2+} ($\mu g\ cm^{-2}$)	Ca^{2+} ($\mu g\ cm^{-2}$)
6 M	PTF1	2.06	0.37	3.22	35.85	1.21	6.92	6.73	55.01
12 M	PTF2	24.16	14.49	42.95	19.10	<LOD	4.95	1.07	45.81
18 M	PTF3	200.48	179.85	319.62	110.00	<LOD	34.43	14.51	244.98
24 M	PTF5	28.34	27.53	14.75	9.75	1.56	4.99	1.49	65.68

Table A5.2 Concentration of soluble ions measured in passive filters exposed in Ferrara for 6, 12, 18 and 24 months. <LOD means below limit of detection.

EXP. TIME	SAMPLE	Cl^- ($\mu g\ cm^{-2}$)	NO_3^- ($\mu g\ cm^{-2}$)	SO_4^{2-} ($\mu g\ cm^{-2}$)	Na^+ ($\mu g\ cm^{-2}$)	NH_4^+ ($\mu g\ cm^{-2}$)	K^+ ($\mu g\ cm^{-2}$)	Mg^{2+} ($\mu g\ cm^{-2}$)	Ca^{2+} ($\mu g\ cm^{-2}$)
6 M	SMF1	17.09	0.97	8.39	7.97	0.39	1.47	1.23	25.29
12 M	SMF2	20.50	9.23	14.15	19.98	<LOD	8.75	2.75	117.57
18 M	PC94	57.80	23.25	25.86	36.43	<LOD	6.05	2.91	76.33
24 M	SMF4	60.55	26.20	38.21	37.66	<LOD	7.41	2.58	144.03

Table A5.3 Concentration of soluble ions measured in passive filters exposed in Florence for 6, 12, 18 and 24 months. <LOD means below limit of detection.

ANNEX 6 – TOTAL SUSPENDED PARTICULATE

	FILTER	TSP ($\mu g\ m^{-3}$)
WINTER 2017	BF11	24.76
	BF12	26.40
	BF13	43.27
	BF14	57.53
	BF15	37.68
	BF16	35.35
	BF17	38.34
SUMMER 2017	BF18	15.53
	BF19	21.13
	BF20	19.66
	BF21	19.64
	BF22	12.03
WINTER 2018	BF23	30.62
	BF24	56.45
	BF25	74.45
	BF26	35.62
	BF27	16.72
	BF28	29.33
SUMMER 2018	BF29	5.75
	BF30	n.a.
	BF31	9.63
	BF32	23.18
	BF33	18.16
	BF34	10.18

Table A6.1 Daily atmospheric concentration of TSP measured in Bologna during different monitoring campaigns. n.a. means not available data.

	FILTER	TSP ($\mu g\ m^{-3}$)
WINTER 2017	PTF11*	18.52
	PTF12*	10.84
	PTF13*	17.73
	PTF14*	18.18
	PTF15*	5.30
	PTF16	10.55
	PTF17*	9.38
	PTF18	5.20
	PTF19	29.04
	PTF20	24.75
SUMMER 2017	PTF_21	23.85
	PTF_22	33.48
	PTF_23	33.81
	PTF_24	23.50
	PTF_25	23.59
	PTF_26	23.66
WINTER 2018	PTF27	31.29
	PTF28	21.14
	PTF29	34.74
	PTF30	46.91
	PTF31	38.64
	PTF32	38.88
SUMMER 2018	PTF33	8.63
	PTF34	10.04
	PTF35	8.26
	PTF36	18.18
	PTF37	19.92
	PTF38	14.42

Table A6.2 Daily atmospheric concentration of TSP measured in Ferrara during different monitoring campaigns.* means that PM monitoring campaign was performed on the roof terrace of Palazzo Turchi di Bagno while the others on the ground floor.

	FILTER	TSP ($\mu g\ m^{-3}$)
WINTER 2017	SMF11	14.75
	SMF12	27.43
	SMF13	19.72
	SMF14	22.93
	SMF15	31.66
SUMMER 2017	SMF16	23.20
	SMF17	26.96
	SMF18	13.03
	SMF19	22.84
	SMF20	18.39
WINTER 2018	SMF21	4.58
	SMF22	25.90
	SMF23	26.84
	SMF24	19.66
	SMF25	14.37
SUMMER 2018	SMF26	18.37
	SMF27	20.30
	SMF28	24.75
	SMF29	16.19
	SMF30	17.78

Table A6.3 Daily atmospheric concentration of TSP measured in Florence during different monitoring campaigns.

ANNEX 7 – WATER-SOLUBLE DATA OF PM MONITORING CAMPAIGNS

	FILTER	Cl^- ($\mu g\ m^{-3}$)	NO_3^- ($\mu g\ m^{-3}$)	SO_4^{2-} ($\mu g\ m^{-3}$)	Na^+ ($\mu g\ m^{-3}$)	NH_4^+ ($\mu g\ m^{-3}$)	K^+ ($\mu g\ m^{-3}$)	Mg^{2+} ($\mu g\ m^{-3}$)	Ca^{2+} ($\mu g\ m^{-3}$)
WINTER 2017	BF11	1.44	2.98	3.07	0.35	0.99	0.18	0.20	1.52
	BF12	1.12	6.88	4.07	0.60	2.51	0.25	0.13	0.99
	BF13	<LOD	12.28	4.05	0.24	3.91	0.26	0.08	0.56
	BF14	<LOD	16.18	4.72	0.25	4.98	0.22	0.06	0.90
	BF15	0.72	7.35	3.79	0.33	2.00	0.19	0.08	0.57
	BF16	<LOD	5.76	2.14	1.94	<LOD	0.14	0.08	1.10
	BF17	0.19	6.27	1.29	0.15	1.49	0.15	0.09	1.05
SUMMER 2017	BF18	0.15	1.01	1.85	0.53	<LOD	0.39	0.01	1.38
	BF19	0.12	1.38	1.82	0.42	<LOD	0.26	0.01	0.81
	BF20	0.41	0.88	2.00	0.42	<LOD	0.30	0.01	0.60
	BF21	<LOD	2.13	2.14	0.08	0.96	0.09	0.03	0.33
	BF22	<LOD	0.51	1.11	0.20	0.24	0.03	0.07	0.14
WINTER 2018	BF23	0.48	6.63	1.25	0.25	1.50	0.12	0.06	1.19
	BF24	0.89	13.42	2.27	0.32	2.92	0.13	0.06	0.68
	BF25	0.95	18.91	3.04	0.43	5.02	0.18	0.08	1.11
	BF26	0.58	10.54	2.06	0.25	2.97	0.14	0.04	0.47
	BF27	0.33	4.88	1.34	0.06	1.53	0.08	0.01	0.33
	BF28	0.56	6.09	1.95	0.14	1.83	0.11	0.03	0.80
SUMMER 2018	BF29	0.03	0.91	0.81	0.08	0.23	0.03	0.03	0.33
	BF30	0.19	0.50	0.40	0.21	0.09	0.02	0.01	0.15
	BF31	0.03	0.39	0.75	0.15	0.17	0.05	0.02	0.16
	BF32	0.00	0.69	0.72	0.07	0.17	<LOD	0.02	0.57
	BF33	0.11	0.47	0.79	0.15	0.18	0.03	0.02	0.40
	BF34	0.03	0.48	0.55	0.11	0.14	0.02	0.02	0.22

Table A7.1 Atmospheric concentration of main soluble ions measured in Bologna during different monitoring campaigns. <LOD means below limit of detection.

	FILTER	Cl^- ($\mu g\ m^{-3}$)	NO_3^- ($\mu g\ m^{-3}$)	SO_4^{2-} ($\mu g\ m^{-3}$)	Na^+ ($\mu g\ m^{-3}$)	NH_4^+ ($\mu g\ m^{-3}$)	K^+ ($\mu g\ m^{-3}$)	Mg^{2+} ($\mu g\ m^{-3}$)	Ca^{2+} ($\mu g\ m^{-3}$)
WINTER 2017	PTF11	0.77	6.48	1.08	0.26	1.84	0.16	0.06	0.41
	PTF12	0.25	3.58	0.96	0.29	0.84	0.21	0.06	0.53
	PTF13	0.91	4.53	1.18	0.32	1.29	0.12	0.08	0.43
	PTF14	0.35	3.19	0.60	0.28	0.61	0.18	0.07	0.44
	PTF15	0.29	1.26	0.83	0.44	0.16	0.38	0.07	0.59
	PTF16	0.21	0.78	0.20	0.16	0.18	0.05	0.02	0.13
	PTF17	1.39	2.72	1.02	2.18	0.40	0.74	0.19	0.80
	PTF18	0.26	0.48	0.24	0.29	0.07	0.09	0.09	0.43
	PTF19	0.85	5.63	0.68	0.44	0.92	0.17	0.18	0.82
	PTF20	1.81	2.51	0.50	0.14	0.25	0.16	0.18	1.51
SUMMER 2017	PTF_21	<LOD	2.55	2.06	0.07	0.74	0.08	0.07	1.02
	PTF_22	0.21	1.52	2.05	0.09	0.73	0.08	0.06	1.08
	PTF_23	<LOD	2.33	3.05	0.12	0.92	0.15	0.08	1.12
	PTF_24	<LOD	1.21	2.05	0.18	0.41	0.03	0.07	0.51
	PTF_25	<LOD	1.39	1.60	0.10	0.62	0.08	0.04	0.34
	PTF_26	0.28	1.35	1.56	0.22	0.41	0.04	0.05	0.52
WINTER 2018	PTF27	0.45	5.82	2.66	0.11	1.62	0.17	0.10	1.15
	PTF28	0.23	2.52	0.68	0.11	0.70	0.05	0.04	0.68
	PTF29	1.03	2.32	0.58	0.45	0.53	0.13	0.10	1.39
	PTF30	1.08	6.70	0.92	0.53	1.26	0.33	0.11	1.32
	PTF31	0.54	6.67	1.00	0.23	1.57	0.23	0.08	0.88
	PTF32	1.15	5.41	0.98	0.47	1.29	0.21	0.10	1.05
SUMMER 2018	PTF33	0.84	0.43	0.47	0.54	0.08	0.02	0.06	0.32
	PTF34	0.08	0.53	0.51	0.18	0.12	0.02	0.03	0.24
	PTF35	0.13	0.30	0.34	0.14	0.11	0.01	0.02	0.14
	PTF36	0.06	0.34	0.42	0.05	0.17	0.03	0.02	0.37
	PTF37	0.00	0.90	0.58	0.03	0.30	<LOD	0.02	0.34
	PTF38	0.03	0.22	0.27	0.02	0.10	0.01	0.02	0.24

Table A7.2 Atmospheric concentration of main soluble ions measured in Ferrara during different monitoring campaigns. <LOD means below limit of detection.

	FILTER	Cl^- ($\mu g\ m^{-3}$)	NO_3^- ($\mu g\ m^{-3}$)	SO_4^{2-} ($\mu g\ m^{-3}$)	Na^+ ($\mu g\ m^{-3}$)	NH_4^+ ($\mu g\ m^{-3}$)	K^+ ($\mu g\ m^{-3}$)	Mg^{2+} ($\mu g\ m^{-3}$)	Ca^{2+} ($\mu g\ m^{-3}$)
WINTER 2017	SMF11	0.78	3.15	2.21	0.61	0.55	0.26	0.10	1.53
	SMF12	0.37	2.73	2.06	0.37	0.55	0.17	0.08	1.51
	SMF13	0.20	0.86	0.53	0.23	0.10	0.18	0.05	1.39
	SMF14	0.51	1.67	0.53	0.34	0.29	0.31	0.06	1.16
	SMF15	0.36	2.27	0.73	0.35	0.40	0.30	0.06	1.42
SUMMER 2017	SMF16	1.05	0.68	1.17	1.23	<LOD	0.42	0.03	1.67
	SMF17	2.57	1.11	1.16	2.30	<LOD	0.50	0.05	1.51
	SMF18	0.37	0.46	1.10	0.42	<LOD	0.28	0.03	0.78
	SMF19	0.12	0.65	0.91	0.38	<LOD	0.17	0.01	1.14
	SMF20	0.13	0.39	1.08	0.38	<LOD	0.22	0.03	1.05
WINTER 2018	SMF21	0.05	0.16	0.06	0.03	0.03	0.02	0.00	0.14
	SMF22	0.09	0.84	0.20	0.03	0.12	0.05	0.02	1.91
	SMF23	0.19	1.37	0.38	0.14	0.18	0.10	0.03	1.45
	SMF24	<LOD	0.33	0.22	0.02	0.09	0.01	0.02	1.74
	SMF25	0.63	0.85	0.32	0.34	0.19	0.05	0.04	0.63
SUMMER 2018	SMF26	0.04	0.29	0.60	0.06	0.17	0.02	0.02	1.03
	SMF27	0.03	0.39	0.91	0.07	0.25	0.02	0.02	0.74
	SMF28	0.02	0.33	0.99	0.04	0.26	0.03	0.02	0.74
	SMF29	0.02	0.25	0.59	0.05	0.19	0.02	0.02	0.54
	SMF30	0.02	0.30	0.63	0.06	0.18	0.03	0.02	0.62

Table A7.3 Atmospheric concentration of main soluble ions measured in Florence during different monitoring campaigns. <LOD means below limit of detection.

ANNEX 8 – PUBLICATIONS, PROCEEDINGS, PRESENTATIONS

Publications

Durability assessment to environmental impact of nano-structured consolidants on Carrara marble by field exposure tests

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HIGHLIGHTS

- Cultural heritage increasingly at risk due to climate change impact
- Need of compatible and resilient consolidating products for marble
- Carrara marble models (treated and not) exposed at four European sites
- Rain principally affected the durability of $CaCO_3$-precursor consolidants.

GRAPHICAL ABSTRACT
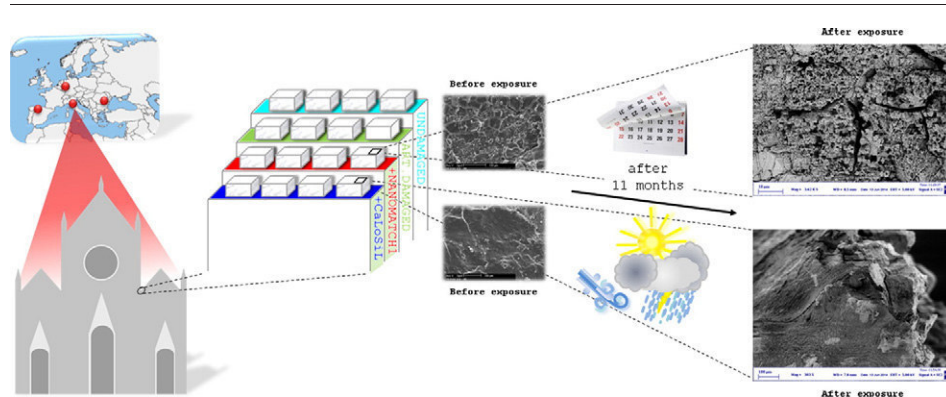
ARTICLE INFO

ABSTRACT

The EU policy of reducing the emissions of combustion generated pollutants entails climate induced deterioration to become more important. Moreover, products applied to preserve outdoor built heritage and their preliminary performance tests often turn out to be improper. In such context, the paper reports the outcomes of the methodology adopted to assess the durability and efficiency of nano-based consolidating products utilized for the conservation of carbonate artworks, performing field exposure tests on Carrara marble model samples in different sites in the framework of the EC Project NANOMATCH. Surface properties and cohesion, extent and penetration of the conservative products and their interactions with marble substrates and environmental conditions are here examined after outdoor exposure for eleven months in four different European cities and compared with the features of undamaged and of untreated damaged specimens undergoing the same exposure settings.

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1. Introduction

The intensification of climate changes combined with the recent reduction in acidic air pollution in urban areas has made climate conditions to become more influential in the weathering of outdoor built heritage (Grossi et al., 2008). In this regard, research has been specifically devoted in the last decades by the European Union to assess the effects of environmental changes, including climatic ones, on cultural heritage and to develop mitigation strategies aiming at its protection and conservation (Kucera et al., 2005; Grossi et al., 2007; Sabbioni et al., 2007; Watt et al., 2009; Franzen et al., 2011; Bernardi et al., 2012; Sabbioni et al.,

2012; Ashley-Smith et al., 2013; Ozga et al., 2014). In particular, available projections on climate change impact on cultural heritage have evidenced that decohesion and fracturing of carbonate stone, widely encountered in archaeological and historic built heritage, are likely to increase in Europe in the near (2010–2039) and the far future (2070–2099) induced mainly by (i) surface recession, (ii) thermal stress and (iii) salts crystallization (Bonazza et al., 2009a, 2009b; Grossi et al., 2011). Several efforts have been made since the 20th century in order to re-establish the original physical-mechanical properties of deteriorated stone and to increase their durability by the extensive use of both organic and inorganic consolidants. It is widely known that the performance and long-term efficiency of organic consolidants have been heavily reconsidered as they frequently undergo irreversibility of the treatments and chemical modifications caused by the interaction with both the environmental conditions and the substrate (Melo et al., 1999; Amoroso, 2002; Favaro et al., 2006, 2007). Although traditional inorganic consolidants as well as innovative nanomaterials (mainly dispersion of barium/calcium/magnesium hydroxide nanoparticles in alcohol) display better physical-chemical compatibility with carbonate stones and good chemical stability to environment, improvements should be introduced in order to ensure higher cohesive effect and better penetration into the porous matrix of damaged substrate (Camaiti, 2000; Giorgi et al., 2000; Amoroso, 2002; Doehne and Price, 2010; Chelazzi et al., 2013; Natali et al., 2014). In addition, possible interactions between the developed material and the outdoor environment should be evaluated, as pollution and weathering factors may act on the new product as well as on the historic substrates. In this regard, most of the studies have been carried out in laboratory, in accelerated and controlled environment. Unfortunately, climate simulation chamber is not designed to accurately replicate the real conditions of outdoor environment failing in the simulation of the synergetic action of environmental parameters as well as their variations at short and long time scale. Higher correspondence to the reality is although achieved by field exposure tests. Hence the need to define the most suitable ageing tests arises whenever resistant and compatible conservative materials are designed. In literature, most of field trials were performed to study damage mechanisms on building materials induced by weathering or pollutants (Zappia et al., 1998; Viles et al., 2002; Urosevic et al., 2012) or to evaluate new products' performance through their application directly on historic damaged substrate, with the risk to be sometimes unsuitable and irreversible applications (Favaro et al., 2005, 2006, 2007; Varas et al., 2007). On the contrary, field tests on model samples allow to evaluate the features of the examined product in response to different environmental conditions and to improve its performance without any damage to the works of art. Nevertheless, still scarce examples of published results on this issue are available (Simon and Snethlage, 1996).

In this paper we discuss the results obtained by performing field tests of model samples in Carrara marble exposed at four European monuments (Santa Croce Basilica in Florence, Cologne Cathedral, Oviedo Cathedral and Stravopoleos Monastery in Bucharest) in order to study the compatibility and environmental durability of the consolidating product developed within the EC Project NANOMATCH (Bernardi et al., 2012). The product's performance is also tested in comparison to CaLoSiL® and its consolidating use in the conservation of cultural heritage discussed. Because of the rising role of climate parameters in causing damage to heritage building materials and the expected increase of surface recession of carbonate stones due to rainfall, the samples under study were placed in unsheltered areas directly exposed to precipitation events. The integration of the results here presented with those carried out in laboratory as part of the EC NANOMATCH Project provided complete information on applicability, compatibility, efficiency and durability of the tested conservative products and allowed to identify and subsequently manage the possible drawbacks before their application on works of art.

2. Materials and methods

2.1. Investigated conservative products

Preliminary tests and application trials were performed to identify the proper alkaline earth alkoxide among those synthesized for consolidating carbonate stones to evaluate the most suitable methodology for its production at industrial scale and to optimize the application parameters (Favaro et al., 2008; Duchêne et al., 2012; Ossola et al., 2012; Favaro et al., 2014; Natali et al., 2015). The best results were obtained with nano-solution of calcium tetrahydrofurfuryloxide (Ca(OTHF)2) (NANOMATCH1) in 1:1 ethanol:ligroin at 20 g/L of calcium, applied by brush on quarried Carrara marble samples for two times on one surface (Natali et al., 2015). In order to compare the performance of the new consolidating agent, CaLoSiL® (IBZ-Salzchemie GmbH & Co.KG), product widely employed for stone consolidation, was selected and applied by brush on other samples. In CaLoSiL®, particles of calcium hydroxide were dispersed in ethanol at 20 g/L of calcium. The consolidating effect of these products is produced by calcium carbonate, obtained by the reaction of calcium hydroxide and calcium alkoxide with atmospheric moisture and carbon dioxide. Since both NANOMATCH1 and CaLoSiL® are precursors for the deposition of calcium carbonate, they could be effectively employed to treat carbonate substrates.

2.2. Field tests

We tested the compatibility and environmental durability of NANOMATCH1 and CaLoSiL® on Carrara marble, a metamorphic stone primarily composed of calcite crystals. Polished marble plaques with dimensions of 10 cm × 10 cm × 5 cm were placed outdoor in an unsheltered area, exposed to rain wash-out, in four European sites characterised by different meteorological and climatological conditions:

- Santa Croce Basilica in Florence (Italy);
- Cologne Cathedral (Germany);
- Oviedo Cathedral (Spain);
- Stavropoleos Monastery in Bucharest (Romania).

A stainless metallic rack, perforated and tilted with 30° slope, supported the samples and allowed the drainage of rainwater (Fig. 1). Field trials lasted for eleven months in each site, from April/May 2013 to March/April 2014.

In order to obtain a stone substrate characterised by a heavy intergranular decohesion, part of samples was previously artificially damaged by thermal stress (i.e. exposed at 600 °C for 1 h), which led to a total structural disintegration of Carrara marble (Bourguignon et al., 2014). Indeed, the anisotropy of calcite in thermal response leads Carrara marble to be affected by thermoclastism and therefore to granular

Fig. 1. Carrara marble model samples exposed on the rack at Santa Croce Basilica, Florence.

disaggregation and material exfoliation (Bonazza et al., 2009b). The experimental exposure included the evaluation and comparison of Carrara marble samples (i) sound (undamaged), (ii) artificially damaged by thermal stress, (iii) damaged and treated with NANOMATCH1 and (iv) damaged and treated with CaLoSiL®. An overall description of the methodological approach adopted is given by Natali et al. (2015), which reports also some of the preliminary results obtained.

2.3. Climatological characterisations of sites

The sites selected for exposure tests of stone models are characterised by different environmental conditions. All of them are urban areas and therefore their atmospheric composition is influenced by the gases and aerosol, including nanoparticles, emitted by stationary and mobile combustion sources (vehicular traffic, domestic heating/cooling systems and industries). Yearly air quality data for each site are reported in Natali et al. (2015). Following the Köppen-Geiger's climate classification (Kottek et al., 2006), Florence has a humid subtropical climate (Cfa), slightly influenced by the Mediterranean one (Csa). Precipitations are more pronounced in the intermediate seasons and in winter while the summer is dry (http://worldweather.wmo.int/); relative humidity values fluctuate between 65% and 76%. Cologne and Oviedo are characterised by warm damp temperate climate with warm summer (Cfb) (Kottek et al., 2006). Precipitations are abundant throughout the year and lead the average value of relative humidity to remain always above 75% (http://www.climatemps.com/). Bucharest belongs to the warm damp temperate climate with hot summers (Cfa) (Kottek et al., 2006) since the presence of the Carpathians Mountains (northward) and of the Black Sea (southward) mitigate the humid continental climate typical of south-eastern Europe. Precipitations are frequent in spring and modest during the other seasons; mean relative humidity therefore ranges from 65% to 85%.

During the eleven months of field tests, Florence and Bucharest showed the same temperature range in summer, with August as the hottest month (high average daily temperature of 31–33 °C), while in winter the Romanian city is cooler (reaching 12 consecutive days with temperatures strictly below freezing from the end of January and the beginning of February and simultaneously recording many snowfalls) (https://weatherspark.com/). Cologne and Oviedo show a general lower temperature in summer than the previous cities while considering the cool season Oviedo displays the mildest winter among all the exposure sites, hardly reaching the 0 °C. As reported by Natali et al. (2015), Florence and Oviedo experienced the highest monthly rain amounts (respectively 144 mm in October in Florence and 152 mm in November in Oviedo) as well as the highest cumulative amounts during the exposure period (both around 820 mm); the total mm of rainfall are lower in Cologne (460 mm) and Bucharest (275 mm). Moreover, the number of events of heavy rain (i.e. when precipitation rate is equal or >25 mm/day following Bradley and Jones, 1995) particularly hazardous for the preservation of carbonate stone were also taken into consideration. During the eleven months of exposure, Florence experienced 5 *heavy rain events* mainly during winter months, and 12 *medium rain events* (i.e. when rain rate is between 10 and 25 mm/day following Bradley and Jones, 1995) spread in summer (http://www.weatheronline.co.uk/). Also Oviedo was characterised by 8 *heavy rain events* during the exposure time, sometimes more than one per month. By contrast, these events turned out few (3) but intense in Bucharest, reaching even 70 mm/day, while almost absent in Cologne (http://www.weatheronline.co.uk/).

2.4. Analytical techniques

During the research work we investigated (i) the aesthetical properties (ii) surface cohesion of treated samples (iii) the distribution of the consolidants (iv) their surface penetration and interactions with both Carrara marble substrates and environmental agents by means of the following analyses:

- Quantitative colour evaluation of samples carried out by a portable spectrophotometer Konica Minolta CM-700d to measure CIE$L^*a^*b^*$ coordinates for the definition respectively of luminosity (L^*) and chromaticity coordinates (a^* and b^*) according to the UNI 8941: 1987 Standard Colored surfaces (1987). The data here presented are the average values of measurements repeated three times on the same selected area. The total colour difference (ΔE^*) between two measurements has been calculated from CIE$L^*a^*b^*$ coordinates $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, and its perception by human sight and the threshold of acceptability was evaluated according to the classification supplied by Miliani et al. (2007).

- Optical Microscopy (OM) and Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) to investigate the morphology and microstructure of samples as well as the distribution of the applied conservative products. Observations of polished cross and thin sections of samples were performed by using a petrographic microscope Olympus BX 51 equipped with a scanner PRIMOPLUS 32. SEM-EDX investigation was carried out with a ZEISS 1530 instrument equipped with a dispersive X-ray analyser on bulk samples and polished cross sections coated with a thin gold layer.

- Scotch Tape Test (STT) or "peeling test" following the standard protocol procedure published by Drdácký et al. (2012) for the quantitative assessment of the cohesion of samples surface. Pressure-sensitive tape was applied at the investigated area and the amount of the material detached from the surface after the tape removal was quantified by weight. Each test was repeated 10 times in the same area of the selected stone sample. Moreover, two different areas in the same sample have been selected for the test to be conducted before and after exposure.

- Capillary water absorption measurement performed according to the standard UNI EN 15801:2010, 2010, in order to evaluate the amount of water absorbed by a specimen per surface unit (Q_i) over time. Q_i (kg/m^2) is defined as $Q_i = (m_i − m_0) / S$ where S is the surface of the specimen in contact with water, m_i and m_0 are the weights of the specimens measured during the test at time t_i and t_0 respectively. The capillary water absorption coefficient (WAC) is the slope of the linear section of the curve obtained plotting the mass change per area (Q_i) versus the root of time ($t_i^{1/2}$).

- Ultrasonic pulse velocity determination, carried out in accordance with the standard EN 14579, 2004, was measured using ultrasonic non-destructive digital indicator tester (PUNDIT) with an emitting frequency of the instrument transducer of 60 kMHz and a measurement resolution of 0.1 μs. The measurement was conducted in direct mode putting the two probes on two parallel surfaces of specimens (one treated and the opposite), where a thin layer of oil is previously applied to optimize the contact between the specimen and the probe. For each specimen the measurement has been carried out three times and the average results with the relative standard deviation have been reported.

Samples were analysed before treatment, after treatment/before exposure and after eleven months of exposure in order to investigate the surface properties and cohesion, as well as to estimate the extent of the penetration for both the conservative products, considering their interactions with marble substrate and environmental conditions. In addition, results obtained by analysing treated samples before exposure were compared with those obtained on sound and artificially damaged samples in order to verify the potential improvement of the physical-mechanical properties after treatment and the aesthetical compatibility of the treatment as well.

3. Results and discussion

3.1. Colorimetric characterisation of samples

The granular disintegration of marble samples due to thermal stress led to a general increase of all colorimetric parameters, causing a variation in total colour visible by human sight and above the threshold of

Table 1
Variation of colorimetric CIE$L^*a^*b^*$ parameters and of total colour (ΔE^*) between 1) artificially damaged samples and sound ones (before exposure); 2) treated samples and artificially damaged ones (before exposure); 3) treated samples after and before exposure.

			Florence	Cologne	Oviedo	Bucharest
Art. damaged samples - sound samples (before exposure)	ΔL^*		6.44	4.16	4.65	6.38
	Δa^*		0.94	0.86	0.97	0.60
	Δb^*		2.31	3.13	3.74	1.98
	ΔE^*		6.92	5.27	6.04	6.71
Treated samples - art. damaged (before exposure)	ΔL^*	NANOMATCH1	−0.10	−0.49	−0.59	−0.29
		CaLoSiL®	0.20	0.31	0.73	2.44
	Δa^*	NANOMATCH1	−0.20	0.01	−0.24	−0.01
		CaLoSiL®	0.06	0.40	0.03	0.01
	Δb^*	NANOMATCH1	0.87	1.02	0.80	1.21
		CaLoSiL®	−2.22	0.53	−1.17	−1.60
	ΔE^*	NANOMATCH1	0.92	1.14	1.02	1.25
		CaLoSiL®	2.40	2.12	1.38	2.92
Treated samples after exposure – treated samples before exposure	ΔL^*	SOUND	1.64	0.52	1.16	−3.05
		ART. DAMAGED	−4.19	−5.19	−4.88	−9.26
		NANOMATCH1	−3.81	−3.23	−4.61	−6.45
		CaLoSiL®	−1.08	0.04	−2.76	−4.00
	Δa^*	SOUND	0.38	0.25	1.33	0.52
		ART. DAMAGED	0.78	0.42	0.93	0.73
		NANOMATCH1	0.83	0.25	0.93	0.49
		CaLoSiL®	0.02	−0.38	0.27	0.09
	Δb^*	SOUND	0.94	1.02	1.33	2.15
		ART. DAMAGED	4.26	1.54	1.62	3.22
		NANOMATCH1	2.46	−0.05	1.50	1.00
		CaLoSiL®	2.76	−0.98	2.42	1.59
	ΔE^*	SOUND	1.93	1.17	1.85	3.77
		ART. DAMAGED	6.03	5.43	5.22	9.83
		NANOMATCH1	4.62	3.42	4.94	6.54
		CaLoSiL®	2.98	2.43	4.25	1.56

acceptability (i.e. $\Delta E > 5$) (Miliani et al., 2007), as shown in Table 1, where the results of all the variation of colorimetric CIE$L^*a^*b^*$ parameters and of total colour (ΔE^*) are summarized. In particular, artificially damaged samples showed a whitening effect ($\Delta L^* > 0$) induced by an increase in surface reflectivity and a shift toward the yellow component ($\Delta b^* > 0$). Analysing data acquired after the application of conservative products, NANOMATCH1 entails a small increase in the yellow component while CaLoSiL® induces a slight whitening of samples surface. In any case, the average values of the total colour differences calculated using colour parameters collected after and before consolidation treatments do not exceed the threshold value of acceptability, showing values below 3 units (Miliani et al., 2007).

The influence of environmental parameters on the chromatic appearance of marble samples was assessed inspecting colour measurement performed after in situ exposure.

Considering samples after and before exposure, Fig. 2 displays that marble artificially damaged exposed at each site shows a visible change in total colour ($5 < \Delta E^* < 10$) that is attenuated by the consolidation treatment. In particular samples treated with CaLoSiL® show $1 < \Delta E^* < 4$ while those treated with NANOMATCH1 present $3 < \Delta E^* < 5$, with the exception of the sample exposed in Bucarest ($\Delta E^* = 7$). Overall, the total colour variation of treated samples remains below the threshold of acceptability (i.e. $\Delta E < 5$) in Florence, Oviedo and Cologne. Analysing the single CIE$L^*a^*b^*$ parameters, the exposure of treated samples led to a slight increase in luminosity and to a small shift of b^* parameter toward the blue component in respect to samples artificially damaged, thus becoming more similar to sound samples.

3.2. OM and SEM observations

OM and SEM investigation evidenced the intra and inter granular decohesion of marble samples as consequence of the thermal stress. The formation of cracks between grains and along their outlines is clearly visible in Fig. 3.

After the application, both NANOMATCH1 and CaLoSiL® were found to cover samples surface with a rather homogeneous layer but neither of them showed deep penetration inside fractures, remaining mainly

Fig. 2. Mean variation of total colour (ΔE^*) of stone samples exposed for eleven months compared with samples before exposure.
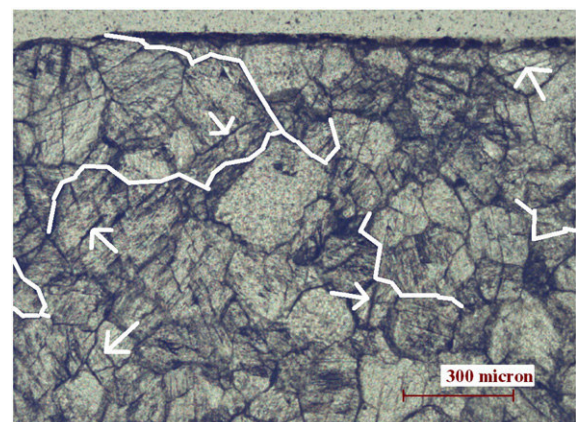
Fig. 3. Micrographs (OM) of thin section in plane polarised light of artificially damaged sample. White arrows indicate intragranular fractures and white lines highlight the presence of intergranular fractures of Carrara marble sample.

on surface or occasionally in the first micrometers of superficial chinks (Fig. 4).

By optical microscopy NANOMATCH1 appeared to be homogeneously distributed on samples surface, with a thickness of about 20–30 μm, which increases where marble surface presents cavities (Fig. 5a). In particular, SEM investigation highlighted that NANOMATCH1 displays a cracked surface (Fig. 4a) similar in the aspect to those formed by TEOS (tetraethoxysilane) based products when applied on stones. TEOS cracked layers on stone surfaces have been observed and extensively described in literature (Miliani et al., 2007; Mosquera et al., 2009). They are typically associated to the TEOS sol gel process in which two reactions (hydrolysis and consequent condensation) take place leading to the formation of a gel in which the solvent is trapped within the silica based network (Mosquera et al., 2009). The cracking occurs during the drying process as consequence of high capillary pressures supported by the gel network. Peruzzo et al. (2016) reviewed the sol gel process occurring in presence of mixture of alkoxides making a detailed description of results obtained by Mass Spectrometry for silicon alkoxides, titanium alkoxides, silicon/titanium alkoxides, germanium alkoxides, tin alkoxides. The formation of a xerogel for NANOMATCH1 after the complete evaporation of the solvent can be hypothesized although any evidences of copolymerization nor sol gel processes for calcium alkoxides are reported (Peruzzo et al., 2016; Turova et al., 2002).

The consolidation with CaLoSiL® caused instead the formation of a compact layer on all the surface of samples (Fig. 5b). This layer, generally thicker than that created by NANOMATCH1 application, was detected to reach a maximum thickness of about 40 μm in the hollowed areas of the surface.

Observations by OM and SEM conducted on not treated samples after the exposure in situ displayed calcite grains highly fragmented with rough surface particularly for samples artificially damaged exposed in Oviedo (Fig. 6). In addition sporadic areas covered by a thin layer of secondary calcite were detected both on sound and artificially damaged samples (Fig. 7).

After eleven months of exposure, treated samples underwent a general reduction in the presence and distribution on the surface of both consolidants. Where present, they displayed a decrease in thickness and lost their flat surface, becoming rough and pitted. The loss of consolidants, particularly NANOMATCH1, occurred mainly in samples exposed in Florence and Oviedo, while in Cologne and Bucharest CaLoSiL® was found to remain rather homogeneously distributed (Fig. 8).

3.3. Surface cohesion characteristics (STT)

As already discussed, the thermal stress carried out on samples led to the disaggregation of marble grains caused by the anisotropic behaviour of calcite. A reduction of the cohesive properties is therefore assumed and the amount of material peeled from the surface could be linked to surface cohesive properties of the stone. Taking into account that (i) even a non-consolidated stone may exhibit a decrease in the amount of removed material due to the higher cohesion of the material in the bulk (Drdácký et al., 2012) and (ii) the early peelings might remove dust and not penetrated consolidant, even so the peeling test can give information of cohesive surface properties if the entire trends referred to different sets of samples are compared.

The reduction of the cohesive properties of the samples artificially damaged linked to the disaggregation of marble grains caused by thermal stress was highlighted by the Scotch Tape Test trough an enhancement of the material peeled from the surface of all damaged samples in respect to that removed from sound samples. Following the results obtained by STT it can be also hypothesized that the treatment with both consolidants implied a general increase of cohesion of surface stone samples since the amount of material released from the surfaces of all consolidated samples is lower than that measured from samples subjected to artificial damage. In particular, Fig. 9 displays the weight difference between the quantity of material peeled from the surface of treated samples before exposure and that removed from the surface of artificially damaged samples before exposure (ΔW), showing a higher cohesive behaviour of NANOMATCH1 product (black dots) in respect to CaLoSiL® (white dots).

In Fig. 10 the difference of the amount of incoherent material peeled from the surface of exposed samples at the 4 sites with those removed from samples surface before exposure (ΔW) is presented. Following these results it may be argued that the exposure to the environment of the four European sites caused similar modification of the surface
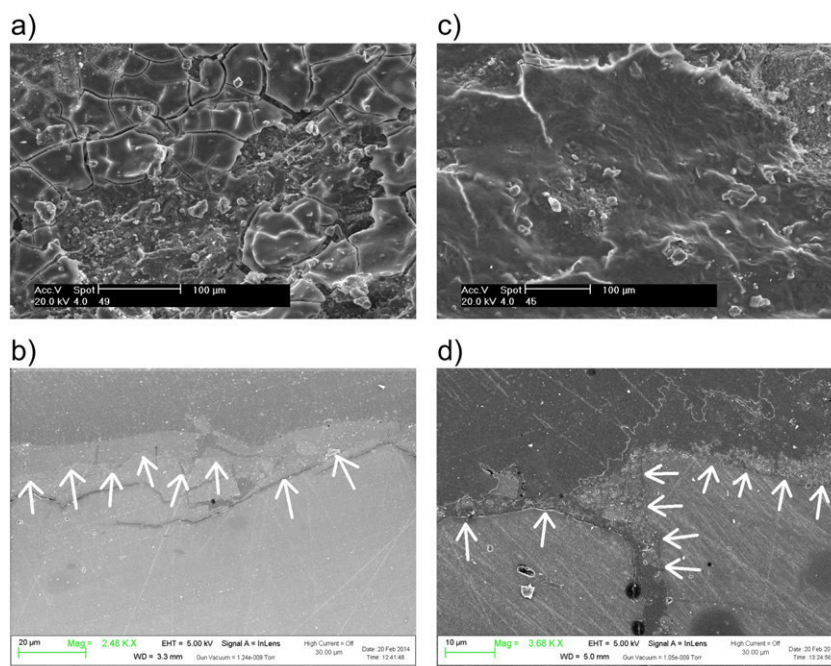
Fig. 4. SEM micrographs of marble samples treated with: NANOMATCH1 product before exposure, bulk sample (a) and polished cross section (b); CaLoSiL® before exposure, bulk sample (c) and polished cross section (d). White arrows highlight the distribution of the consolidants on samples.

a)

b)
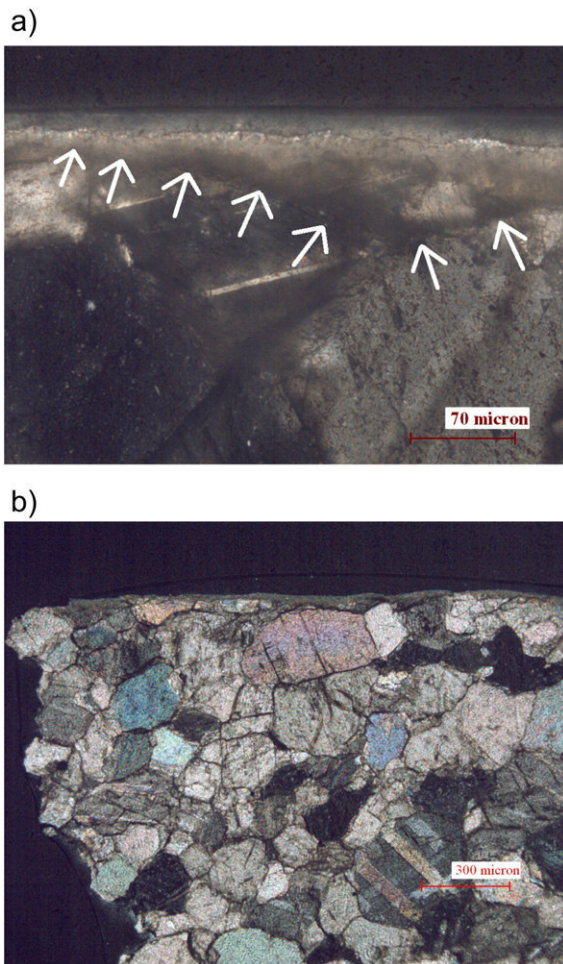
Fig. 5. a) Optical micrographs of thin sections in cross polarised light of sample treated with NANOMATCH1: white arrows indicate the distribution of the surface microcrystalline layer formed after the consolidating treatment. b) Optical micrographs of thin sections in cross polarised light of sample treated with CaLoSiL®.

cohesion in the same classes of samples and a general slight increase in the surface cohesive properties. Specifically, artificially damaged samples show the highest improvement of surface cohesion while the cohesive properties of sound samples and of those treated with CaLoSiL® slightly increase or remain equal to values measured before exposure. On the contrary, the exposure seems to have caused a slight reduction in cohesion of the most superficial part of samples treated with
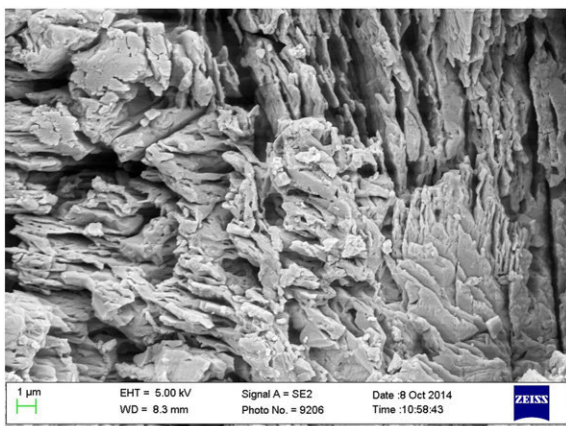
Fig. 6. SEM micrographs of artificially damaged marble sample after exposure in Oviedo.
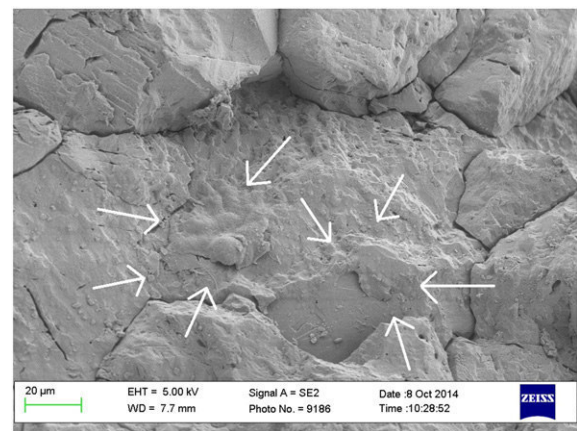
Fig. 7. SEM micrographs of undamaged marble sample after exposure in Oviedo. White arrows highlight the presence of secondary calcite.

NANOMATCH. It can be hypothesized that part of the consolidant surface layer was detached, not adhering to the substrate and therefore removed by the tape during the early peeling.

As evidenced by Drdácký et al. (2012) results of STT can yield to contradictions in the interpretation if not performed in a standardized way and are to be considered reliable only for surface and near-surface layers of the investigated material. Even though the results here presented cannot be ascribed to an effective cohesion or not of the samples in its entirety, the application of the standard protocol published by Drdácký et al. (2012) ensures a correct and reliable understanding of

a)

b)
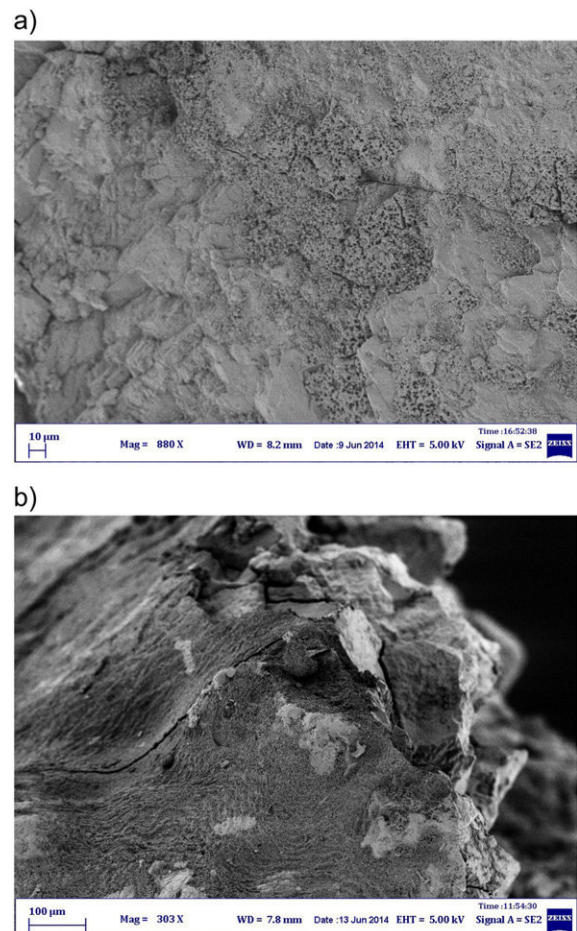
Fig. 8. SEM micrographs of marble samples treated with: a) NANOMATCH1 product after exposure in Florence (bulk sample); b) CaLoSiL® after exposure in Cologne (bulk sample).
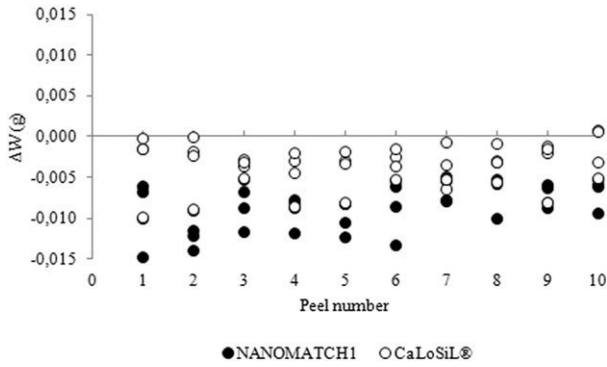
Fig. 9. Weight difference between material peeled from the surface of samples treated with NANOMATCH1 and that removed from the surface of artificially damaged samples (black dots). Weight difference between material peeled from the surface of samples treated with CaLoSiL® and that removed from the surface of artificially damaged samples (white dots). The evaluation considers the samples addressed to all the European exposure sites.

the surface cohesion characteristics of the specimens. Having been the Carrara marble samples treated on one surface by brush application of the consolidating agents, the STT results here presented are to be used for an evaluation of the surface consolidation and strengthening efficiency of the tested treatments.

3.4. Capillary water absorption

Capillarity water absorption test was performed on: i) sound and artificially damaged specimens before and after the exposure; ii) samples artificially damaged and treated with NANOMATCH1 and CaLoSiL® after the exposure. The amount of water (Q_i) absorbed by specimens exposed in the sites of Florence, Cologne and Oviedo is reported in Fig. 11.

Comparing the test results, it is evident that sound specimens absorb less water before than after exposure. Results related to the specimens before exposure show that artificially damaged samples absorb ten times higher amount of water than the sound ones. It is well known that the higher quantity of water taken up is related to the higher open porosity: the additional porosity of damaged specimens disaggregated by thermal stress, as observed by OM and SEM, increases the capillary water absorption. Concerning the effect of consolidation of both tested products, results executed in laboratory as part of the EC
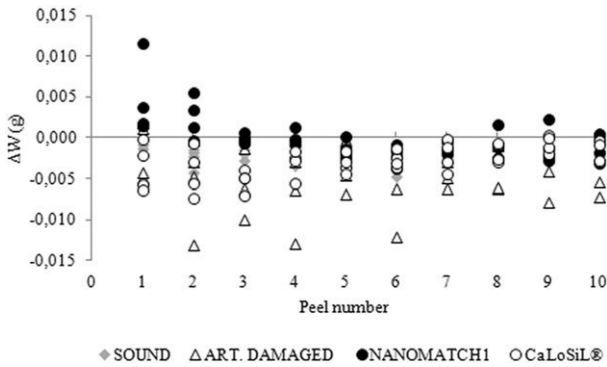
Fig. 10. Weight difference between material peeled from the surface of sound samples after exposure for eleven months in the four European sites and that removed from sound samples before exposure (grey rhombuses). Weight difference between material peeled from the surface of artificially damaged samples after exposure in the four European sites and that removed from artificially damaged samples before exposure (white triangles). Weight difference between material peeled from the surface of samples treated with NANOMATCH1 after exposure in the four European sites and that removed from the same samples before exposure (black dots). Weight difference between material peeled from the surface of samples treated with CaLoSiL® after exposure in the four European sites and that removed from the same samples before exposure (white dots).
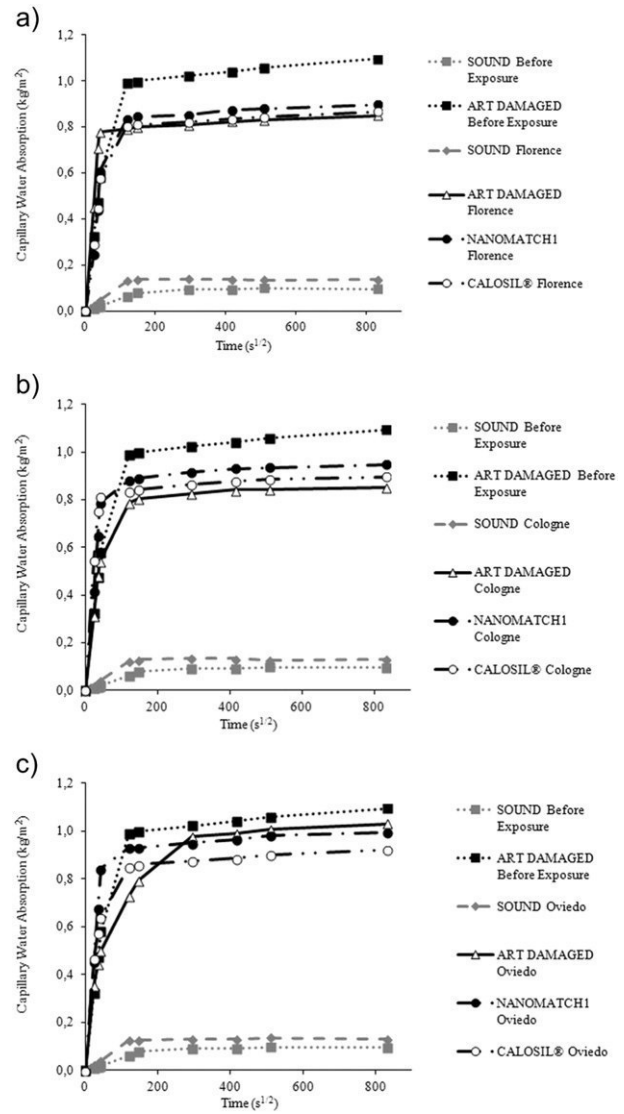
Fig. 11. Capillarity water absorption results referring to: sound and artificially damaged samples before exposure (grey and black squares respectively), sound (grey rhombuses), artificially damaged (white triangles), treated with NANOMATCH1 (black dots) and treated with CaLoSiL® (white dots) samples after exposure in Florence (a), Cologne (b) and Oviedo (c).

NANOMATCH Project demonstrated that the treated specimens presented absorption behaviour (WAC$_{Average}$ = 0.034 kgm^{-2} s$^{-0.5}$ for NANOMATCH1 and WAC$_{Average}$ = 0.027 kg m^{-2} s$^{-0.5}$ for CaLoSiL®) fairly similar to the artificially damaged samples (WAC$_{Average}$ = 0.029 kg m^{-2} s$^{-0.5}$, Bourguignon et al., 2014). Comparing the water absorption capillarity of samples before and after exposure, artificially damaged specimens absorb in general less water after than before exposure, with a similar trend regardless the different site of exposure. This finding is congruent with the STT results obtained, for this class of samples, which highlighted an increase of surface cohesion. Moreover, the outcomes indicate that the different exposure site as well as the conservative products applied (both NANOMATCH1 and CaLoSiL®) do not significantly influence the capillary water absorption. Treated samples with both consolidants exposed in each site show a similar trend of water capillarity absorption.

3.5. Ultrasonic velocity

As for capillarity water absorption test, ultrasonic velocity was performed on: i) sound and artificially damaged specimens before and

after the exposure; ii) samples artificially damaged and treated with NANOMATCH1 and CaLoSiL® after the exposure in Florence, Cologne and Oviedo. The obtained results (Table 2) evidenced a decrease in ultrasonic velocity in the artificially damaged samples (V_{Avg} = 1433 m s^{-1}) with respect to the sound ones (V_{Avg} = 6130 m s^{-1}) before exposure. The measured values after thermal stress indicated that the samples underwent a total structural disintegration following the scale established by Köhler (1988). After the consolidating treatments, average ultrasonic velocity values equal to 1389 m s^{-1} for samples treated with NANOMATCH1 and 1308 m s^{-1} for those treated with CaLoSiL® were detected, slightly lower than those encountered for artificially damaged ones. The measurements for the freshly treated samples here reported were carried out as part of the tests conducted in laboratory within the framework of the EC Project NANOMATCH (Bourguignon et al., 2014). Following the execution of these analyses it has been evidenced higher velocity values near the treated surface with respect to the opposite untreated surface of the samples, which has been interpreted by the Bourguignon et al. (2014) at a first glance as caused by the different content of consolidant in the samples. Nevertheless, since this gradient was also found in artificially damaged samples, it cannot be linked exclusively to a different penetration of the consolidant, but textural inhomogeneity of the stone should also be considered as possible cause. Additionally, Bourguignon et al. (2014) pointed out that the difficulty in drawing sure interpretation concerning the penetration depth of consolidation treatments using ultrasonic velocity measurements is particularly exacerbated when dealing with very low porous lithotype as Carrara marble, even if damaged by thermal stress. After exposure sound samples present a slight decrease in ultrasonic velocity at all analysed sites (V_{Avg} = 5475 m s^{-1}), with values still characteristic of a quarry fresh marble following the scale established by Köhler (1988). This result is in accordance with the study done by Simon and Snethlage (1996)within the framework of the EUROCORE-EUROMARBLE exposure programme, who highlighted how the ultrasonic velocity of the bulk marble material may respond sensibly to the environmental impact in unsheltered conditions already after few months of exposure, even though surface morphological features and colour of stones are more rapidly influenced by environmental conditions being the ultrasonic velocity determined by the internal grain and pore structure. Additionally, they found that marbles with coarse-grained (e.g. Lass marble) presented almost no reduction in ultrasonic velocity because of the exposure, while slight decreases were detected for Carrara marble.

Concerning our results, a decrease was found for artificially damaged samples, particularly evident for those samples exposed in Oviedo, which present V_{Avg} = 584 m s^{-1}. Velocity decreases also for all samples treated with both consolidants exposed in Florence and Oviedo, while a

slight increase is detected for specimens treated with NANOMATCH1 placed in Cologne. It should be pointed out that as a general rule, a scattering of at least 0.5 km s^{-1} should be admitted before changes of us-velocity can be ascribed to enhanced weathering (Sheremeti-Kabashi and Snethlage, 2000).

3.6. Significance of changes at the stone surface due to environmental impact

The analyses conducted under microscope pointed out that in spite of the granular disaggregation caused by thermal stress on Carrara marble samples, both consolidating products remained mainly at the surface of the samples creating an homogeneously distributed layer with higher thickness and compactness in the case of CaLoSiL®. This finding is consistent with the outcomes of the tests performed in laboratory within the framework of the EC project NANOMATCH for verifying the penetration depth of both consolidating agents on diverse lithotypes, including Carrara marble which was found to have a very low overall absorption even if decohesionated (Bourguignon et al., 2014).

The new surface layer formed after the application did not imply negative consequences on the colorimetric parameters with ΔE^* values not exceeding the threshold of acceptability. In spite of the negligible improvement of cohesion of the treated samples in their entirety, detected by ultrasonic velocity measurements, a surface consolidation was achieved as shown by the "peeling test".

The exposure in situ in unsheltered conditions to precipitation impact implied a weathering of all classes of exposed samples causing aesthetic changes generally below the threshold of acceptability, with the exception of the sample treated with NANOMATCH1 exposed in Bucharest, and a loss of the consolidating layers evident mainly in the specimens placed in Florence and Oviedo. Where still present they displayed under scanning electron microscope a clearly weathered morphology and rough and pitted surface. A direct relation between the increase of roughness and loss of material in carbonate stones, mainly low porous, with the rain impact have been evidenced by several authors (Viles, 1990; Simon and Snethlage, 1996; De, 2003; Sabbioni, 2003; Camuffo, 2013). Moreover, the surface recession caused by rain impact, including its clean and acid contribution, has been widely studied and several models and functions have been proposed for its quantification (Lipfert, 1989; Baedecker, 1990; Livingston, 1992; Webb et al., 1992; Tidblad et al., 2001; Kucera et al., 2007). In reviewing the existing functions, performed with the aim of their application for the production of scenarios of climate change impact on the surface recession of marble and limestone, Bonazza et al. (2009a) underlined the driving role of clean rain (the so-called karst effect) in determining the quantity of materials loss due to precipitation. This weathering phenomenon is naturally exacerbated in polluted areas because of an additional rain acidity due to the presence of sulfuric and nitric acid and of the dry deposition of gaseous pollutants (SO_2 and NO_X). In addition to the chemical dissolution process, the mechanical effect of rain needs also to be taken into consideration, which may significantly increase the surface recession especially in porous carbonate materials with high surface roughness during events of heavy precipitation (Camuffo, 2013). Simon and Snethlage (1996) during the EUROCORE-EUROMARBLE exposure programme found that the interaction between carbonate stones and incident rainfall produces clear morphological alterations even within a short term of exposure and higher rates of surface recession are found in sites affected by highest annual precipitation amount. Our results are in line with these outcomes having evidenced a major loss of consolidating agents in those sites characterised by the highest monthly rain amounts and frequency of heavy rain events (Florence and Oviedo). As both NANOMATCH1 and CALOSIL® are precursor of calcium carbonate, calcite and vaterite are the only two possible mineral phases expected to crystallize within stone porosity following their application, making them susceptible to chemical dissolution by rainfall. Besides the dissolution of the carbonate matrix, it is widely known

Table 2
Ultrasonic velocity measured in Carrara marble samples. V_1, V_2, V_3 (m s^{-1}) indicate three different measurements carried out on the same samples and their average value is expressed as V_{Avg} (m s^{-1}). Standard deviation (s.d.) is also reported.

SAMPLE	V_1 (m s^{-1})	V_2 (m s^{-1})	V_3 (m s^{-1})	V_{Avg} (m s^{-1})	s.d.
Sound_before exposure	6098	6410	5882	6130	265.4
Art. damaged_before exposure	1441	1453	1405	1433	24.9
Sound_Cologne	5484	5313	5313	5370	98.9
Sound_Florence	5426	5484	5484	5464	33.7
Sound_Oviedo	5568	5568	5632	5590	37.0
Art. damaged_Cologne	1302	1323	1295	1307	14.3
Art. damaged_Florence	1345	1273	1319	1312	36.1
Art. damaged_Oviedo	589	584	580	584	4.7
NANOMATCH1_Cologne	1443	1431	1435	1436	6.2
NANOMATCH1_Florence	1158	1216	1189	1188	28.8
NANOMATCH1_Oviedo	944	939	946	943	3.6
CaLoSiL®_Cologne	1416	1333	1302	1351	59.1
CaLoSiL®_Florence	1129	1116	1142	1129	12.7
CaLoSiL®_Oviedo	1126	1121	1111	1120	7.8

that as consequence of rainfall impact, precipitation of secondary calcite can occur as the water evaporates at the surface with formation of new low porous and hard calcareous crusts (calcrete) on carbonate stones (Dever et al., 1987; Cassar, 2002) Rainwater saturated with carbon dioxide acts in fact as an acid dissolving calcite and then redeposits it as a precipitate on the surfaces of the soil particles. The formation of a layer of secondary calcite observed by scanning electron microscope (Fig. 7) may be reasonably attributed to this phenomenon and constitutes a reliable explanation of the slight increase in the surface cohesive properties of the exposed samples, particularly artificially damaged ones detected by the "peeling test".

4. Conclusions

As consequence of the predicted increase over the 21st century of surface recession on carbonate materials, a deep understanding of the performance of conservative products in responding to environmental impact is essential for setting up suitable strategies of cultural heritage safeguard.

By performing filed exposure tests, the work presented allowed to investigate the effect of climate parameters, particularly rainfall, on Carrara marble in different state (quarry fresh, total structural disaggregated, treated with NANOMATCH1 and CaLoSiL®) exposed in four European sites with diverse environments. The conditions of exposure were set up and the analyses selected and conducted with the main purpose of exploring the surface changes occurring on Carrara marble samples i) after the application of the consolidating products and ii) before and after exposure. Moreover the innovative consolidating product synthetized in the framework of the EC Project NANOMATCH was tested in field.

Both conservative products were found to remain mainly on surface and did not penetrate deeply in the substrate. This implied only a surface cohesion of samples pointing out that the examined products behaved as protectives agents or surfaces of sacrifice rather than consolidants.

Following the exposure in situ a loss of the consolidating layers was found mainly for the samples exposed in the sites characterised by the highest monthly rain amounts and frequency of heavy rain events.

Further investigations are suggested in order to improve the penetration of the products taking into consideration the best environmental conditions and techniques of application, the proper materials to be treated and the most appropriate solvent. Following our results in fact it may be argued that marble substrates are not suitable materials to be treated with the tested consolidants, while porous limestones should be perhaps preferred. Additional studies should be also carried out in order to better characterise NANOMATCH1 product as well as to clarify which processes lead to the formation of the cracked layer observed on stone surface by SEM technique.

Acknowledgements

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FIELD EXPOSURE TESTS TO EVALUATE THE EFFICIENCY OF NANO-STRUCTURED CONSOLIDANTS ON CARRARA MARBLE

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Abstract

In the context of a changing environment, the preservation of outdoor built heritage is increasingly threatened. Furthermore the application of conservation products does not always achieve the expected results. Furthermore, preliminary tests aimed at evaluating the performance of new products often show them to be inappropriate. In such situations, the paper reports the outcomes of an innovative methodology adopted to assess the efficiency and durability of nano-based consolidating products utilized for the conservation of carbonate artworks, carrying out field exposure tests on Carrara Marble model samples in different sites. Surface properties, superficial cohesion, distribution and penetration of the conservation products and their interactions with substrates and environmental conditions were examined and compared with the features of undamaged samples and of artificially damaged samples.

Keywords: Carrara marble, field exposure tests, consolidating treatment, metal alkoxide, nano-based materials

1. Introduction

The intensification of climate changes in the last century is seriously affecting the conservation of outdoor built heritage (Sabbioni *et al.*, 2012). In particular, available projections have evidenced that temperate Europe will likely undergo an increase in loss of cohesion of carbonate stones (widely encountered in archaeological and historic built heritage) because of higher impact of (i) surface recession, (ii) thermal stress and (iii) salts crystallization (Grossi *et al.*, 2008, 2011; Bonazza *et al.*, 2009a, 2009b). Several consolidating as well as protective agents, both organic and inorganic, have been widely employed since the 20th century in order to reduce the impact of the environment on original substrates but unfortunately their performance and long-term efficiency often proved to be questionable (Amoroso, 2002; Favaro *et al.*, 2006, 2007; Doehne and Price, 2010; Giorgi *et al.*, 2000). The recent introduction of nanomaterials as consolidating agents for carbonate materials seems positively contributing to the conservation of cultural heritage (Giorgi *et al.*, 2000; Chelazzi *et al.*, 2013; Natali *et al.*, 2014) but further developments of appropriate preliminary tests aimed at evaluating the durability in real conditions of new products are necessary as pollutants and weathering factors may act on the new product as well as on the historic substrates.

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This paper reports the results of an innovative methodological approach adopted to evaluate the efficiency, compatibility and durability of nano-based consolidating agents used for the conservation of cultural heritage, performing field exposure tests on Carrara Marble model samples exposed to different environmental conditions.

2. Materials and methods

The consolidating products trialled in this work are nano-based precursors for the deposition of calcium carbonate: calcium tetrahydrofurfuryloxide $(Ca(OTHF)_2)$, hereafter indicated as NANOMATCH1, and CaLoSiL[®] (IBZ-Salzchemie GmbH & Co.KG) (Natali *et al.*, 2015). NANOMATCH1 is a nano-solution of calcium alkoxide in 1:1 ethanol:ligroin at 20 g/L of calcium, synthesized by EU NANOMATCH Project aimed at developing a family of innovative materials for the consolidation of historical substrates (Bernardi *et al.*, 2012; Favaro *et al.*, 2014). The performance of the new consolidating product is here compared with that of CaLoSiL[®], nano-particles of calcium hydroxide dispersed in ethanol at 20 g/L of calcium, which is already widely employed for stone consolidation.

The efficiency and durability of NANOMATCH1 and CaLoSiL[®] were tested on quarried plaques of Carrara Marble (dimensions 10×10×5cm). Polished marble samples were exposed for eleven months outdoor to the direct action of rainwater on stainless metallic racks, perforated and tilted to allow the drainage of water (Natali *et al.*, 2015). Four European sites characterised by different environmental condition were selected to host the exposure of samples: Santa Croce Basilica in Florence (Italy), Cologne Cathedral (Germany), Oviedo Cathedral (Spain) and Stavropoleos Monastery in Bucharest (Romania). Some samples were previously artificially aged by thermal stress (600°C for 1 hour) in order to get the same compactness of exposed real samples since calcite crystals deform anisotropically upon heating (Bonazza *et al.*, 2009b; Sassoni and Franzoni, 2014; Andriani and Germinario, 2014). Field trials compare the performance of Carrara Marble samples (i) undamaged, (ii) artificially damaged by thermal stress, (iii) damaged and treated by brush with NANOMATCH1 and (iv) damaged and treated by brush with CaLoSiL[®].

In order to evaluate and compare the features of different samples and to understand the possible influence of various environmental conditions, samples underwent the following analyses before treatment, after treatment/before exposure and after eleven months of exposure:

- Optical microscopy (OM) using a petrographic microscope Olympus BX 51 on thin and polished cross sections to analyse the microscopic features of marble samples before and after exposure and to verify the presence and the extent and condition of the tested consolidants;
- Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDS) utilizing a ZEISS 1530 instrument on bulk samples and polished cross sections to better understand the microscopic features of samples and treatments;
- Colorimetric Analyses performed with a portable spectrophotometer Konica Minolta cm-700d/600d and according to the CIELAB system and the norm ISO 7724-1:1984 for quantitative colour evaluation of samples;
- Capillary Water Absorption (CWA) test in agreement with the Italian standard UNI EN 15801:2009;

- Scotch Tape Test (STT), following the procedure published by Drdácký *et al.* (2012) for the quantitative assessment of the cohesion of samples surface.

3. Results and discussion

OM and SEM analyses clearly show a reduction in cohesion of marble samples as consequence of thermal expansion. NANOMATCH1 is detectable as a microcrystalline layer rather homogeneously distributed on samples surface, with a thickness of about 20-30 µm, which increases in the hollowed areas of the surface (Fig. 1).
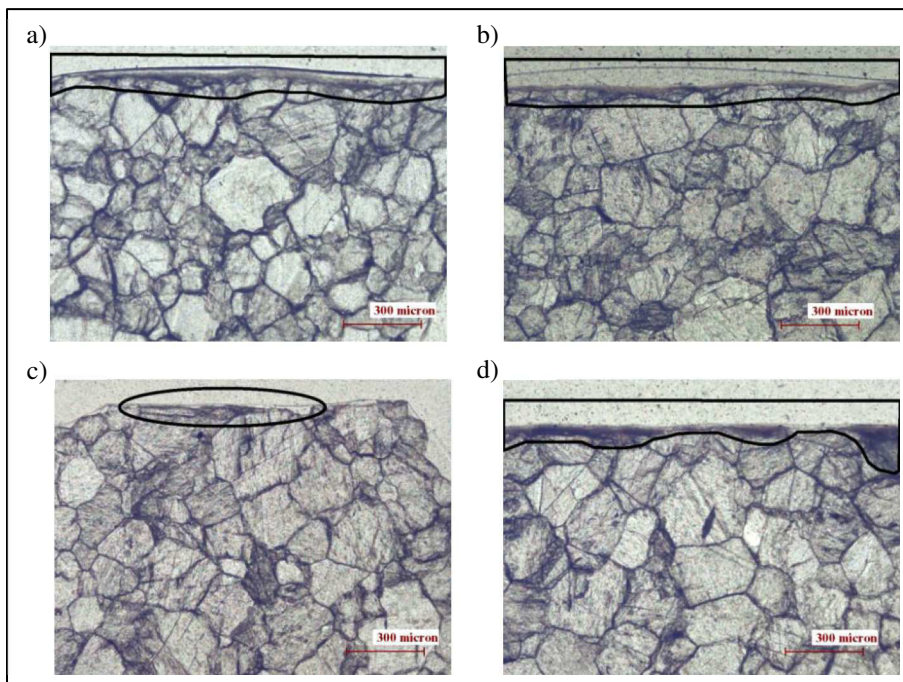
Fig. 1: Optical Micrographs (plane-polarized light) of sample treated with:
a) NANOMATCH1 before exposure; b) CaLoSiL® before exposure; c)NANOMATCH1after the exposure in Florence; d) CaLoSiL® after exposure in Cologne. Black lines highlight the presence of the consolidating products.

Moreover, SEM results display that the new consolidating product has a cracked surface probably caused by too rapid evaporation of solvent, or improper environmental conditions under which the reaction happened. By contrast, the consolidation with CaLoSiL® leads to the formation of a more compact layer on the surface of all samples, distinguished by higher thickness values (Fig. 1). Anyway, both treatments remain mainly on surface or occasionally in the first micrometres of superficial chinks, as observable under OM and SEM. OM and SEM analyses carried out after exposure highlight a general increase in cracks and a loss of material on surface of all kinds of samples. It can be argued that the exposure to weather conditions and atmospheric pollutants may have weakened the stone substrate and solubilised the calcite by acid rain impact (Camuffo, 2013). In support of the hypothesis of chemical decay by precipitation, Fig. 2 shows the presence of rough and

pitted surface on treated samples. Additionally, the appearance of turbid, brownish portions in some cracks near the sample surface (observable by OM) may suggest the incomplete washout of the solubilised material and its partial penetration and re-precipitation inside chinks as microcrystals or in amorphous form. Results also show that the distribution and durability of the applied products after exposure were influenced by the kind of treatment and environmental conditions of each exposure site. In effect, NANOMATCH1 is present only in traces in all four European sites while generally the detectable amount of CaLoSiL® is higher. Furthermore the conservation products were more heavily detached and damaged in Florence and Oviedo than in Cologne and Bucharest: although the city of Florence and Oviedo are characterised by different climatic conditions, it was observed that both were affected by heavy rain events during the eleven months of exposure (Natali *et al.*, 2015). Therefore the mechanical erosion of intense rain may have enhanced the normal solubilisation of the applied consolidating products due to karst effect and acid rain. Nevertheless, where present, NANOMATCH1 and CaLoSiL® seem to be effective in preserving the stone substrate.
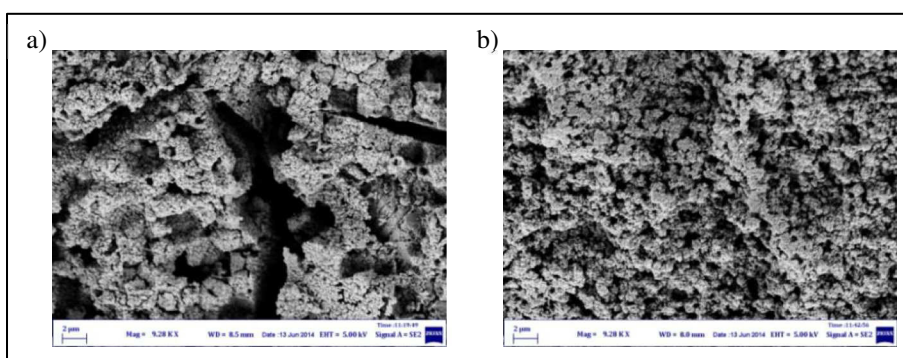
Fig. 1: SEM micrographs of marble samples treated with NANOMATCH1 (a) and CaLoSiL® (b) after exposure in Cologne.

The results of colorimetric analyses show that the application of NANOMATCH1 and CaLoSiL® caused a variation of total colour (ΔE^*) deemed not perceptible by human sight (i.e. $\Delta E^* < 5$), according to indications given by Garcìa and Malaga (2012) (Fig. 3). Comparing colour measurements carried out before and after exposure, artificially damaged samples exposed in each site display the highest and visible change in total colour ($5 < \Delta E^* < 10$) while the application of consolidating products on marble samples sought to preserve a chromatic appearance of the substrate as much as possible similar to that of an exposed undamaged marble. Indeed, apart from samples treated with NANOMATCH1 and placed in Bucharest, the exposed treated samples did not exceed the threshold of perceptibility ($\Delta E^* = 5$; Fig. 3).

Considering the results of capillary water absorption, an increase in open porosity is detectable as a consequence of thermal damage. However the treatments with NANOMATCH1 and CaLoSiL® do not influence the porosity of samples. Also, exposure at the different sites does not affect the capillary water absorption.
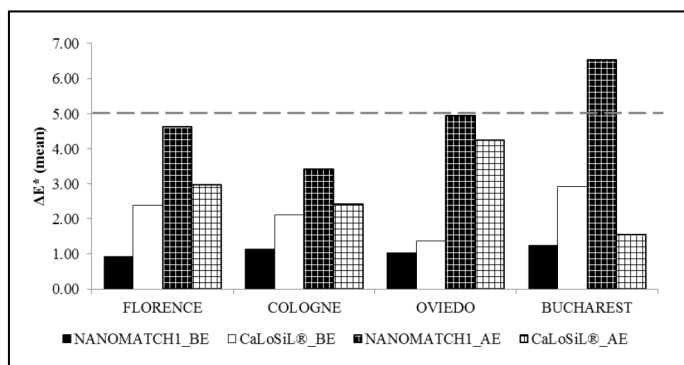
Fig. 3: Total colour variation (ΔE*) before and after the application of treatments; and before (BE) and after (AE) exposure in each site. The dotted line indicates the threshold of perceptibility by human sight.

The disintegration of marble grains induced by thermal stress and perceptible by microscopic investigations is confirmed by the peeling tests. The material released from the surface of artificially damaged samples is more than that removed from undamaged samples. After the application of NANOMATCH1 and CaLoSiL®, the amount of material peeled from treated samples is less than that removed before treatment, demonstrating the consolidating property of the products. In particular, NANOMATCH1 displays better cohesive performance than CaLoSiL®. The comparison between the amounts of material removed from the surface of exposed samples with those peeled from samples before exposure shows a general reduction, and is similar for each class of samples of all tested sites. Artificially damaged samples display the highest enhancement of cohesion, most probably due to the solubilisation and recrystallization inside cracks of $CaCO_3$ induced by rain. Concerning treated samples, good results emerged from samples treated with CaLoSiL®: an increase in cohesion is detectable in all peeling test steps, as shown in Fig. 4 for samples located in Florence.
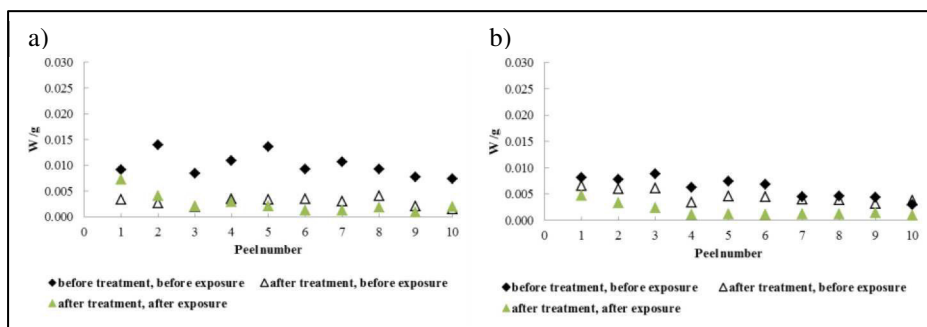
Fig. 4: Scotch tape test data referred to samples artificially damaged treated with NANOMATCH1 (a) and CaLoSiL® (b) and exposed in Florence.

Exposed samples treated with NANOMATCH1 underwent a slight reduction in cohesion in the most superficial part, with a gain in compactness in the inner portion of surface (Fig. 4). It can be supposed that the likely removal of parts of conservation products induced by

environmental factors should cause the exposure of marble damaged by thermal stress but not yet strengthened by the action of rain.

4. Conclusions

The paper has presented and discussed the outcomes of the study concerning the performance of consolidating products on marble samples before and after exposure in different sites. NANOMATCH1 and CaLoSiL® showed good chemical compatibility with the Carrara Marble on which were applied since both are precursors for calcium carbonate. Their application leads to the formation of microcrystalline layers rather homogeneously distributed on samples surface that occasionally penetrates in superficial cracks. Therefore NANOMATCH1 and CaLoSiL® increased the compactness of only samples surface as detected by scotch tape test, without acting as strong structural consolidants for low porosity material such as marble. The aesthetical appearance and the porosity of the marble samples were scarcely altered by the treatments.

The methodological approach utilized in this project proved to be useful in assessing the performance and durability of the products in different environmental conditions, characteristic of each selected site. Field exposure tests gave the possibility to evaluate the environmental impact on the studied substrate and the applied conservation actions. Results of analyses performed after exposure highlighted the importance of precipitations (in terms of acidity and pattern) in the deterioration of the applied conservative products. Acid rain as well as heavy rain events seems to be decisive in the increase of the natural dissolution of $CaCO_3$ induced by karst effect. Moreover the results of the scotch tape test confirmed that generally the exposure of samples resulted in a partial dissolution of $CaCO_3$ and recrystallization within the stone matrix. Nevertheless, colorimetric features of samples as well as their porosity were not significantly influenced by the exposure in different cities.

Testing using longer duration of exposure seems recommendable in order to provide conditions more similar to the real behaviour of conservation products applied on cultural heritage. Moreover improvements of the preparation procedure, penetration and strengthening effect of the new calcium alkoxide product are suggested to increase its performance as consolidant.

Acknowledgements

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Abstract:	In spite of the widely recognized negative effect of air pollution on stone used in historic built heritage located in urban areas and the numerous studies internationally developed on this topic, gaps still remain in measuring deposition fluxes on architectural surfaces and developing proper tools for short and long-term management of cultural heritage in polluted areas in a changing environment. Two-years long field exposure tests with model samples are currently under execution in Italian cities characterized by different environmental conditions as a non-invasive methodological approach for investigating the impact of urban pollution on carbonate stones (marble and limestone). Several analytical techniques (both physical and chemical) are used for characterising the state of degradation of the exposed stone specimens while aerosol monitoring campaigns allow to compare the atmospheric components with those actually accumulate on samples surface. After a description of the methodological approach of this study and a general environmental characterisation of each selected site, results of aerosol monitoring campaigns (including bioaerosol) and colorimetric analyses performed during the first year of exposure in Bologna are here presented and discussed.

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A multidisciplinary study of air pollution impact on stone in urban sites

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Abstract

In spite of the widely recognized negative effect of air pollution on stone used in historic built heritage located in urban areas and the numerous studies internationally developed on this topic, gaps still remain in measuring deposition fluxes on architectural surfaces and developing proper tools for short and long-term management of cultural heritage in polluted areas in a changing environment.

Two-years long field exposure tests with model samples are currently under execution in Italian cities characterized by different environmental conditions as a non invasive methodological approach for investigating the impact of urban pollution on carbonate stones (marble and limestone). Several analytical techniques (both physical and chemical) are used for characterising the state of degradation of the exposed stone specimens while aerosol monitoring campaigns allow to compare the atmospheric components with those actually accumulate on samples surface. After a description of the methodological approach of this study and a general environmental characterisation of each selected site, results of aerosol monitoring campaigns (including bioaerosol) and colorimetric analyses performed during the first year of exposure in Bologna are here presented and discussed.

1. Introduction

Air pollution is an outstanding issue that affects mainly urban areas and that entails serious consequences not only for human health and environment but also for the conservation of cultural heritage. Indeed, stone decay induced by atmospheric pollution still remains a current problem in urban environment, with remarkable cultural and economic consequences. The decay of built heritage leads to an irreversible loss of value of works of art as well as requires expensive restoration and conservation works. Therefore, it is necessary to fully

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investigate the main causes of damage and deterioration processes of cultural heritage in order to plan specific actions of preventing conservation.

Historically, wet and dry deposition of sulphur dioxide (SO_2) along with particulate matter (PM) has been recognised to be the major cause of stone surface deterioration in terms of soiling and blackening, implying both unaesthetic effect and chemical and physical consequences to stone substrate [1, 2]. In particular, the reaction of SO_2 with carbonate stones (*e.g.* marble and limestone) can lead to the formation of gypsum crusts through sulphation process in partially sheltered areas while carbonaceous particles, deriving from combustion processes, entail the darkening of architectural surfaces and the catalysis of SO_2 oxidation process [3].

It is noteworthy that the concentration of SO_2 has decreased from the mid-20th century and this reduction is expected to continue also in the future thanks to mitigation policies, improvements to industrial plants and use of low-sulphur fuels [4]. On the contrary, emissions from vehicular traffic have recently become the main responsible of pollution detected in the majority of western European cities and the continuous demand for transport likely suggests an eventual growth of pollutants from mobile sources, such as ozone, nitrogen oxides and particles richer in organic compounds [5]. This change in emissions sources has possible consequences also in the degradation of cultural heritage, as modern and future soiling is likely dominated by organic compounds and nitrate salts that increase biological colonisation and favour a shift towards warmer tones of architectural surfaces [5-8].

The effects of multipollutants on carbonate stones have already been studied mainly analysing samples collected directly from monuments and historic buildings [9-14] and secondly by tests in simulation chamber, in order to assess the role of different parameters with potential impact in deterioration phenomena [2, 15-16]. In addition, field exposure tests are increasingly gaining more importance as they supply a more realistic comprehension of the on-going damage and allow simultaneous analyses on different materials and/or in diverse climate conditions [1, 17-23]. Even if the combination of these approaches has promoted a better comprehension of the deterioration phenomena on cultural heritage caused by the impact of pollution and has improved air monitoring of the surrounding environment, gaps still exist mainly in the correlation between the amount of a specific air pollutant and its impact on building materials through dose-response functions.

In this regard, the Institute of Atmospheric Sciences and Climate of the National Research Council of Italy (ISAC-CNR, Bologna) and the Department of Physics and Earth Sciences of the University of Ferrara are collaborating to assess the effect of urban atmospheric pollution on mainly carbonate sedimentary and metamorphic stones by performing field exposure tests for 24 months in Italian cities characterised by different environmental conditions (*i.e.* Bologna, Ferrara and Florence). The project aspires specifically to quantify the deposition fluxes of certain components (soluble and carbon fractions) of atmospheric particulate on selected stone samples, in order to analytically assess their contribution to aesthetical and chemical damage of carbonate surfaces. In order to characterise the state of degradation of the exposed surfaces, several analytical techniques, both physical and chemical, are used for. In this context, besides Colorimetric Analyses on the exposed surface of stone samples, the deposit collected from stone specimens undergo Ion Chromatography and Elemental Analysis-Isotope Ratio Mass Spectrometry of carbon every 6 months and these results are compared with

soluble ions and carbon fractions detected every 6 months during weekly aerosol monitoring campaigns performed in each site. Moreover, for an exhaustive characterisation of the deposited matter and its interaction with the stone substrate, the analytical method will be implemented at the end of 2 years of exposure with Scanning Electron Microscopy equipped with Energy Dispersive X-Rays Spectroscopy and Inductively Coupled Plasma Mass Spectrometry of the deposited particulate matter and Optical Microscopy on thin polished sections of stone plaques. Moreover, bioaerosol monitoring campaigns were performed in Bologna at 6 and 12 months of the study in order to determine the atmospheric concentration of the potentially biodeteriogenic air-dispersed viable components.

In particular, the present paper aims to describe the methodological approach chosen for this research, arisen from a careful combination of field exposure tests, aerosol monitoring campaigns and laboratory analyses. Moreover, a general environmental characterisation of each selected urban site is here presented as well as results of aerosol monitoring campaigns and colorimetric analyses performed during the first year of exposure in Bologna are reported and discussed.

2. Material and methods

2.1. Exposure tests setup

217 samples of Carrara Marble (CM, 163 samples) and Nembro Limestone (NL, 54 samples) were prepared as polished tablets with dimensions of 12x12x2 cm in order to be exposed outdoor for field tests and further samples were prepared as reference materials. These lithotypes were selected for their almost totally carbonate composition and because they have been widely used as construction and decorative materials in cultural heritage since ancient time. CM is a medium-fine grained metamorphic stone extracted in Apuan Alps (Tuscany), characterised by a white colour with some thin grey veins and patches. On the contrary, NL is a nodular rose limestone with several red stylolitic joints and calcite veins; it represents the lower stratigraphic unit of the Rosso Ammonitico Veronese formation, extracted from Valpolicella area (Veneto). CM has been exposed in Bologna, Ferrara and Florence in order to test the same lithotype in diverse environmental conditions, while NL in Ferrara for comparing how two different stones react to the same environmental parameters. In particular, samples have been exposed outdoor, partially sheltered by direct rain, in urban areas strongly affected by pollution due to vehicular traffic but at a height suitable to avoid a direct contact with exhaust gases from vehicles. Therefore, the exposure has been performed on: i) a terrace at the first floor of the National Research Council of Italy (CNR) in Bologna (via P. Gobetti 101), ii) on a roof terrace of Turchi di Bagno Palace in Ferrara (nowadays used by the University of Ferrara), oriented towards the rather busy Via Porta Mare at around 6 m high from the ground level, and iii) in a loggia of San Marco Museum overlooking via G. La Pira in the centre of Florence (Figure 1). Galvanized metallic racks were purposely built to host samples with three different exposure orientations: horizontal, oblique (tilted with 45° slope) and vertical, in order to test how positioning may influence particle deposition and its potential removal by wind-driven rain. Specifically, samples have been exposed in a way that the material deposited on the exposed surface of a whole

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sample and mechanically collected following the procedure explained by Bonazza *et al.* [22] can be analysed every 6 months to detect carbon fractions and another one for soluble ions. Furthermore, other two specimens, dedicated for further analyses, will remain exposed for the complete period, as sketched in Figure 1. A roof was properly added to racks placed in Bologna and Ferrara to provide a partial protection from precipitation. The experimental tests started in June/July 2016 and they will finish after two years, even if samples exposure was designed in order to extend the study for further months. At the same time, 10 quartz fibre filters have been exposed horizontally in each site for 2 years for monitoring atmospheric particulate matter every 6 months (in terms of soluble and carbon fractions).

Furthermore, aerosol monitoring campaigns were planned in the same locations every 6 months in order to monitor the atmosphere close to samples racks and compare it with the material actually deposited on stone surface.

2.2. Analyses

Environmental conditions of each site were first investigated to compare similarities and differences among the selected areas and to better understand trend of main pollutants and their major sources. For this reason, data from the public network of monitoring stations managed by ARPAT (Tuscany Region Environmental Protection Agency) in Florence and ARPAE (Emilia-Romagna Region Environmental Protection Agency) in Ferrara and Bologna were used. We selected pollutants monitored in each site for at least 20 years and potentially harmful for the conservation of cultural heritage. Therefore, mean annual data of PM_{10}, NO_2 and SO_2 collected by urban background and traffic-oriented stations located close to our exposure site are processed and compared (Table 1).

Among the selected sites, Bologna was selected for a detailed aerosol investigation, including the biological component, and thus this work focus on outputs of aerosol monitoring campaigns and colorimetric analyses acquired during the first year in this site.

Aerosol monitoring campaigns were performed close to the exposed samples for a week every 6 months, with a sampling time-period of 60 min alternated with 30 min of rest during weekdays and vice versa in the weekend. Each filter started to collected aerosol in the morning (around 10 a.m.) and finished at the same time of the following day. Total suspended particulate (TSP) was collected using a SACOGFAS system working at a flow-rate of 40 Lmin^{-1} with prewashed and prebaked quartz fibre filters with diameter of 47 mm. Once sampled, different analyses were performed on some punches of exactly known area taken from the filters. On a first punch water-soluble ions were analysed by an ICS-1000 Ion Chromatograph (Dionex). Anions analysis was carried out by means of a IonPac AS14A (Dionex) column using 8 mM Na_2CO_3 /1 mM $NaHCO_3$ as eluent at 1 mL min^{-1} flow rate and, for the detection, a conductivity system equipped with a ASRS-ULTRA suppression mode (Dionex). Cations determination was performed by means of a CS12A (Dionex) column using 20 mM MSA as eluent at 1 mL min^{-1} flow rate and, for the detection, a conductivity system equipped with a CSRS-ULTRA suppression mode (Dionex). More details on samples preparation are reported in Piazzalunga et al. 2013 [24]. A second punch was analysed by a thermo-optical transmittance (TOT) method

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with a Sunset Laboratory OC/EC analyser in order to provide organic and elemental carbon concentrations [24-26].

Contemporarily to aerosol monitoring campaigns, bioaerosol was assessed and quantified in Bologna at 6 and 12 months of the study. Surface Air System (SAS), in combination with laboratory culture methods [27, 28], was selected as sampling method to determine the atmospheric concentration of the potentially biodeteriogenic airborne viable components. In particular, culture media suitable for the colonisation of bacteria (Plate Count Agar-PCA, Oxoid Standard, USA) and fungi (Sabouraud Dextrose Agar with chloramphenicol - SDA, Oxoid, USA) were selected. Each sampling (20 s) was conducted in double (2 PCA and 2 SDA) and repeated in the morning and the afternoon utilizing a SAS Super 100 (International PBI, Milan, Italy), characterised by a flow rate of 100 litres of air per minute, and Petri dishes of 90 mm. After sampling, plates containing the specific culture medium remained in incubators at 25°C and 22°C (for fungi and bacteria, respectively) for 5-7 days for the growth of microorganisms and the developed colonies were counted, adjusted by the correction table supplied by PBI and calculated as colony-forming units per volume of sampled air (CFU m^{-3}). Furthermore, a morphological analysis was performed on fungal colonies [27].

Aesthetical features of exposed lithotypes surface have been investigated every 6 months by colorimetric analysis and compare to colorimetric parameters of stones before exposure. This analysis was carried out by a portable spectrophotometer Konica Minolta CM-700d to measure CIEL*a*b* coordinates for the definition respectively of luminosity (L*), chromaticity coordinates (a* and b*) and total colour difference (ΔE*), according to UNI 15886:2010 [29]. Surface of samples designed for colorimetric analysis were divided in 4 quarters so as to measure colour on only one quarter every six months, repeating the analysis for 5 times in 5 different points. The spectrophotometer has a measurement geometry of d/8° with a xenon light source with UV cut filter, a silicon photodiodes array detector and measures an area of 8 mm. Colour data are assessed for the D65 illuminant, with the observer at 10° and including the specular component of light.

3. Results and discussion

3.1. Environmental characterisation

Locations selected for exposure tests are Italian urban areas with different size: from medium city with a population between 100000 and 300000 (Ferrara) to big cities with 300000-1000000 inhabitants (Bologna and Florence).

The selected sites are characterised by warm temperate climate with hot summer, among which Florence shows drier summer. However, the cumulative annual precipitation is higher in Florence than in Bologna and in Ferrara (see Table 2). Their mean annual temperature ranges between 13 °C and 15 °C even if Florentine winters are generally milder than Ferrara and Bologna. Mean annual relative humidity is generally high in all sites (around 70 %).

Bologna and Ferrara are located in the Po Valley, a densely populated area of Northern Italy characterised as a hot spot in Europe to air quality. The wide diffusion of industrial activities, road transport, farming and

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breeding as well as orographic conditions, which favour weak circulation, entail air stagnation and transformation of pollutants into secondary compounds. Also topographical configuration of Florence (a closed basin, encircled by hills) along with high traffic intensity favour recurrent heavy pollution episodes. However, a clear decrease of SO_x emissions was observed all over Italy, passing from 1783 Gg in 1990 till to 123 Gg in 2015 [33]. In particular, the mean values acquired by urban traffic-oriented and urban background stations of Bologna, Ferrara and Florence have always been below the detection limit (*i.e.* 14 $\mu g/m^3$) since the beginning of the XXI century [34-35]. Moreover, a general halving of NO_x emissions was estimated at national level between the nineties (2032 Gg) and 2015 (763 Gg) [33]. Analysing NO_2 concentrations measured in the selected sites, even if a gradual decrease has happened over time, mean values of urban traffic-oriented stations located close to stone exposure sites were always higher than those measured by urban background stations, proving a direct impact of vehicular traffic in the emission of this gas. In particular, NO_2 concentration at traffic-oriented stations has always exceeded the limit value fixed for human health protection by the Legislative Decree no. 250/2012 [36] (40 $\mu g\ m^{-3}$) (Figure 2).

Nevertheless, problem related to particulate matter remains still outstanding although the national emissions of PM_{10} underwent a slight decrease from 2000 (225 Gg) to 2015 (179 Gg) but with a not linear and constant trend [33]. Assessing the mean concentrations of PM_{10} measured over years by urban traffic-oriented and urban background stations of Bologna, Ferrara and Florence [34-35], a general reduction is observable and the limit value of annual PM_{10} concentration fixed for human health protection by the Legislative Decree no. 250/2012 [36] (40 $\mu g\ m^{-3}$) has been never exceeded since 2010 (Figure 2). In general, traffic-oriented stations registered higher level than the relative urban background equivalents and above all Ferrara traffic-oriented stations recorded the highest amount of PM_{10} during the last three years of the analysis. Furthermore, the study of the main sources of PM_{10} emissions, performed by the Italian Institute for Environmental Protection and Research [37], highlights that heating system followed by transport are the main responsible in Bologna and Florence while the wide chemical complex in Ferrara entails high emissions along with heating and transport.

Finally, exposure sites assigned to Ferrara and Florence are both located in the old town, close to the city botanic garden and faced to a street rather congested by vehicular traffic (in the case of Florence, this happens even if San Marco Museum is positioned in a controlled traffic zone). On the contrary, CNR of Bologna is just outside the core city, in a residential area: there are a cargo rail network, a congested freeway and highway not far from it and an international airport at almost 3 km distant. Therefore, traffic along with domestic heating during winter are expected to be the major sources of local pollution.

3.2. Aerosol monitoring campaign

Aerosol monitoring campaigns were performed in Bologna in the periods 9-16 February 2017 and 13-19 June 2017, thus representative for cold and warm seasons, respectively. Mean Total Suspended Particulate (TSP) of winter period is more than twice of that detected during summertime (37.62 and 17.60, respectively). Results of ion chromatography relative to both campaigns are listed in Table 3.

In general, nitrates and sulphates are the most abundant anions throughout the selected period while among cations ammonium ion was detected with the highest concentration (Figure 3). Therefore, a relevant concentration of inorganic secondary aerosol was measured over the whole period. In particular, this trend is more pronounced in winter campaign than during the summer one probably due to inversion conditions during cold months that reduce air dispersion capacity of the troposphere as well as because of the presence of more sources of pollutions (*e.g.* domestic heating and congested traffic). Moreover, the strong decrease on NO_3^- in the summer (its average percentage on TSP passed from 22% in winter to 7% in summer) was likely induced by its volatile nature. The relative higher measured concentration of both NH_4^+ and NO_3^- during winter and summer suggests that vehicular traffic could be their major source, as already highlighted in §3.1.

In addition to ion chromatography, carbon speciation was assessed as the impact of carbon fractions on cultural heritage is well documented [1, 9, 38]. Table 3 reports the amount of Organic Carbon (OC) and Elemental Carbon (EC) detected during the sampling periods. EC, also known as black carbon, derives from the incomplete combustion of carbonaceous fuel (*i.e.* traffic and residential heating) while OC could be both biogenic and anthropogenic. In addition to traffic emissions present all year long, biogenic emissions and photo-oxidation processes of gas precursors (secondary aerosol) are the main responsible of OC concentrations during warm season while wood burning and residential heating contribute to winter amount [39-40]. Mean results display an evident predominance of OC over EC in both monitoring campaigns (OC/EC = 8.26 in winter and 10.68 in summer campaign). In particular, OC corresponds to 13% and 19% of TSP on average respectively in winter and summer while EC remained always around 2% of TSP. However, both carbon fractions prevail during winter than in summer in absolute terms likely because of the additional emissions from residential heating [40].

Moreover, further attention was paid to the biological component of aerosol because its study in the field of cultural heritage is connected to the possible alteration processes induced by the growth and metabolic activities of microorganisms, which can colonise both organic and inorganic materials. In the case of stone, the damage can be induced directly by the detected microorganisms or indirectly, as they could behave as biofilm suitable for the growth of other biological organisms more harmful for stone conservation. In this regard, monitoring campaigns of bioaerosol were planned in order to identify the potential biological risk factors for stone conservation.

As shown in Figure 4, total microbial load measured in summer resulted much higher than that detected during the cold period, ranging from 676 CFU m^{-3} to 2387 CFU m^{-3} in warm season and remaining below 350 CFU m^{-3} in winter. Generally, fungi were more abundant than bacteria in both seasons: Total Fungal Load (TFL) were in the range 45-255 CFU m^{-3} and 571-2312 CFU m^{-3} while Total Bacterial Load (TBL) 15-203 CFU m^{-3} and 38-330 CFU m^{-3}, respectively during winter and summer. In particular, *Cladosporium* and *Aspergillus* were identified as the most abundant genera of fungi by the morphological analysis. Therefore, the substantial increase of total microbial load observed in summer has to be induced by higher potential development of fungi colonies. Also mean monthly concentration of fungi spores monitored in Bologna during the period 1999-2016 highlights an increased amount between June and October [41].

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The resulting upgrowth of possible biodeteriogens is likely influenced by favourable environmental conditions, as most microorganisms prefer a temperature between 20°C and 30°C and a relative humidity over 65% [42-43]. In effect, mean temperature changed from 7°C in winter to 27°C during the summer monitoring campaign even if a slight decrease of relative humidity occurred (from 75% in winter to 54% in summer).

Additionally, since biogenic emissions are a source of OC, the increase of microbial load measured during summer could have contributed to the higher concentration of OC detected during summer camping.

3.3. Colorimetric Analysis on stone samples

Sample horizontally exposed in Bologna underwent Colorimetric Analysis after first 6 months. Comparison with the original colorimetric parameters of Carrara Marble highlighted a decreasing rate in lightness and a slight variation of b* parameter towards more positive value while almost no change affected a* parameter (Table 4). Furthermore, L* and b* parameters confirmed higher changes also after 12 months of exposure. This is more evident in the case of samples located horizontally and obliquely while colorimetric parameters of vertically exposed sample remained almost unchanged, as shown in Table 4. In particular, lightness underwent a shift toward more negative values while b* parameter toward the yellow component (Δb*>0). The darkening effect is likely due to the accumulation of carbonaceous fine particles generate by incomplete combustion and therefore elemental carbon represents the main responsible agent [8]. Moreover, literature [8 and related references, 44] highlights that the increasing emissions of organic matter leads to deposits rich in organic materials that are potentially attractive for biological activity and prone to be oxidized. As a consequence, the deposited material exhibits yellowish and brownish colours. Therefore, there could be a relationship between the shift of b* parameter towards more positive values measured on stones surface and the high OC/EC detected during the aerosol monitoring campaigns.

Comparing the variation of total colour, it increased in horizontal samples over time, passing from 5.65 to 7.00. This seems to display as a prolonged exposure entails a higher colorimetric variation of the stone substrate respect to the material just extracted from the cave. After 12 months, also oblique specimen underwent a total colour change similar to that of horizontal sample while vertical specimen remained almost unvaried. This suggests that deposition of particulate happened mainly on horizontal and oblique samples, as expected.

4. Conclusion

In this paper the methodological approach adopted by field exposure tests for assessing the effect of atmospheric pollution on carbonate stone substrates was described. The presented data are a part of the preliminary results of the analyses performed on stone specimens before and after exposure and of aerosol characterization of the sites. In particular, environmental conditions of each site were here described and compared and special attention was drawn to a detailed analysis of the main aerosol components (in terms of soluble ions, carbon fractions and biological load) detected during monitoring campaigns in Bologna during the first year of the study. Finally, changes of colorimetric parameters occurred on Bologna stone specimens after 6 and 12 months of exposure outdoor were shown and discussed.

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Mitigation policies and abatement technology, mainly in industrial facilities, have led to a decrease of SO_2 emissions in all the selected sites while concentrations of NO_2 and PM_{10} remain still remarkable mostly at traffic-oriented monitoring stations. Vehicular traffic heavily affects air quality and it is classified as the first (in Bologna and Florence) or the second (in Ferrara) source of PM_{10}. Focusing on Bologna, aerosol monitoring campaigns confirmed the leading role of traffic in pollution as suggested by the relative high concentrations of NH_4^+ and NO_3^- detected during both studied periods. Nevertheless, atmospheric stagnation and additional pollution sources (*e.g.* heating systems) during wintertime favoured the accumulation of aerosol, detected as higher amount of TSP, soluble ions and carbon fractions respect to summer sampling.

Focusing on carbon speciation, mean results display an evident prevalence of OC over EC in both monitoring campaigns. In particular, OC displays to be more abundant in the summer campaign probably influenced also by higher biomass production. The performed bioaerosol monitoring shows indeed an increase of total microbial load during summer, mainly due to higher potential development of fungi colonies, induced by environmental conditions more suitable for their development and in general for biomass production.

The accumulation of deposited matter influenced the aesthetic appearance of exposed stone samples, mainly of those horizontally and obliquely placed. Especially, lightness underwent a shift toward more negative values while b* parameter toward the yellow component, with an increasing trend over time. These variations could be influenced by carbonaceous particles: EC is recognised to cause blackening of surface while OC a yellowing. This hypothesis may be validated by analysing the carbon components of particles deposited on stone surface and eventually correlating them with colorimetric changes.

Finally, the continuation of aerosol monitoring campaigns and analyses on exposed stone specimens is planned in order to identify the potential risks for cultural heritage induced by air pollution. In particular, this research sets out to:

- characterise the deterioration products coming from the interaction between pollutants and stone substrate in terms of typology, origin and damage caused to stone;
- correlate the deposited soluble and carbon fractions and changes of colorimetric parameters, for setting up damage functions;
- compare the concentrations of pollutants deposited on stone substrate with those present in the atmosphere.

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CAPTIONS:

Figure 1 A) Model of the exposure in field of stone samples. In particular, black squares represent specimens dedicated for carbon speciation, grey ones for ion chromatography and white ones for further analyses. B) Racks hosting stone samples in the loggia of San Marco Museum in Florence.

Figure 2 Mean values of NO_2 (A) and PM_{10} (B) concentration acquired by urban traffic-oriented (solid lines) and urban background (dotted lines) stations of Bologna (circle), Ferrara (square) and Florence (triangle) located close to site selected for exposure test. Green line indicates the yearly limit value for human health protection fixed by Legislative Decree no. 250/2012 [36].

Figure 3 Mean concentration of soluble ions measured during winter and summer 2017 campaigns in Bologna.

Figure 4 Mean daily Total Microbial Load (TML) measured during winter (blue) and summer (red) campaigns 2017.

Table 1 Urban background and traffic-oriented monitoring stations of Bologna, Ferrara and Florence used for pollution characterisation.

Table 2 Climate, geography and some data about population of sites selected for exposure tests [30-32]

Table 1 Atmospheric concentration (μg m^{-3}) of the main ions and carbon fractions measured in Bologna during the 1st year. LOD is calculated as two times the standard deviation of blank filter.

Table 2 Average colour variations ΔL*, Δa*, Δb* calculated between data acquired before and after exposure in Bologna (BO). Values reported represent the average of five measurements carried out on the same quarter of sample repeated for 5 times at the same exposure condition. H = horizontal; O = oblique (slope = 45°); V = vertical; 6m = after 6 months; 12m = after 12 months.
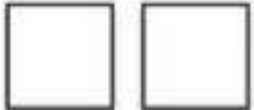
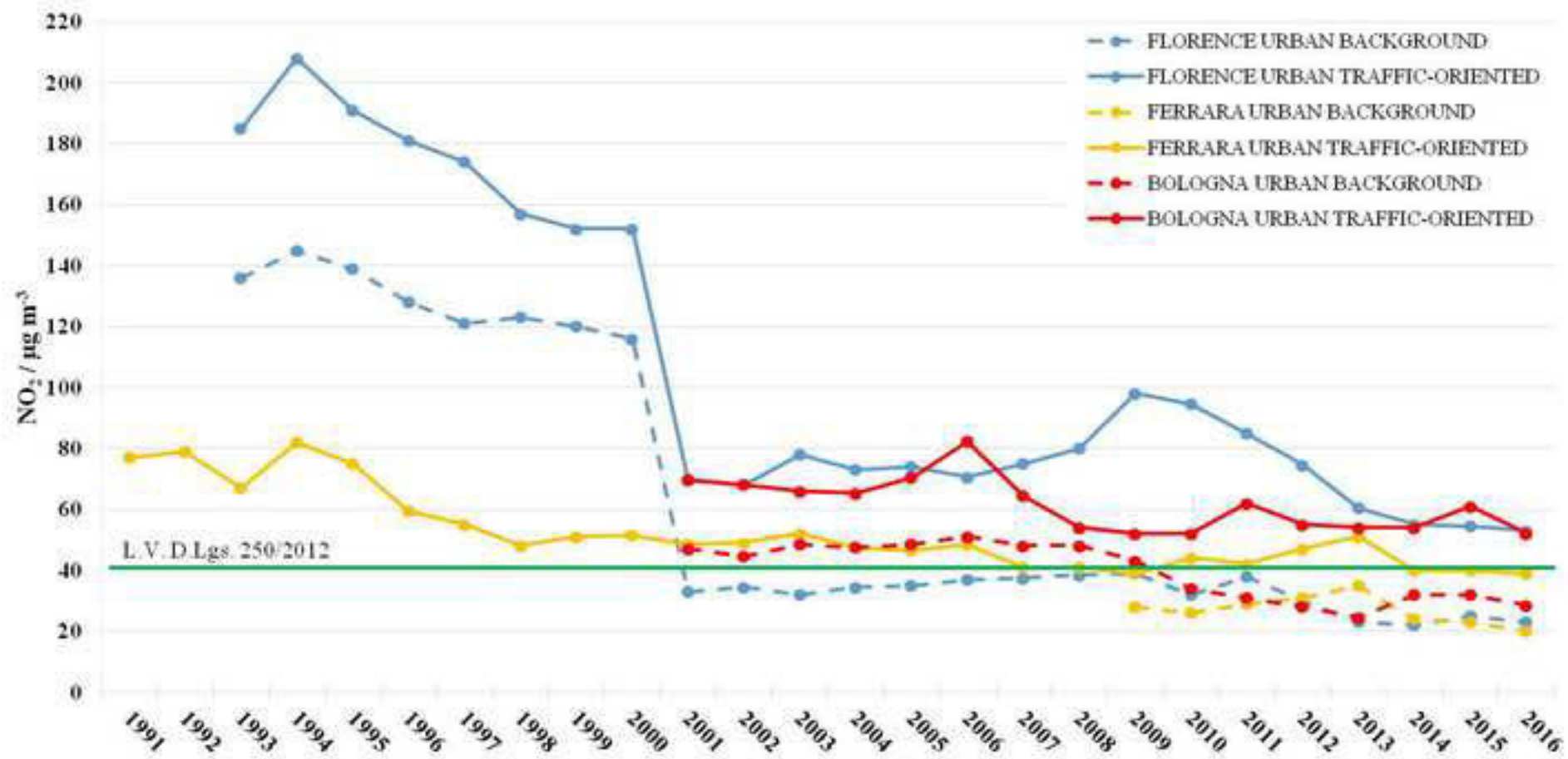| Samples exposure time / Orientation	6 months	12 months	18 months	24 months	24 months
Vertical	■ ▢	■ ▢	■ ▢	■ ▢	□ □
Oblique	■ ▢	■ ▢	■ ▢	■ ▢	□ □
Horizontal	■ ▢	■ ▢	■ ▢	■ ▢	□ □

Figure 2B

Figure 3

Figure 4
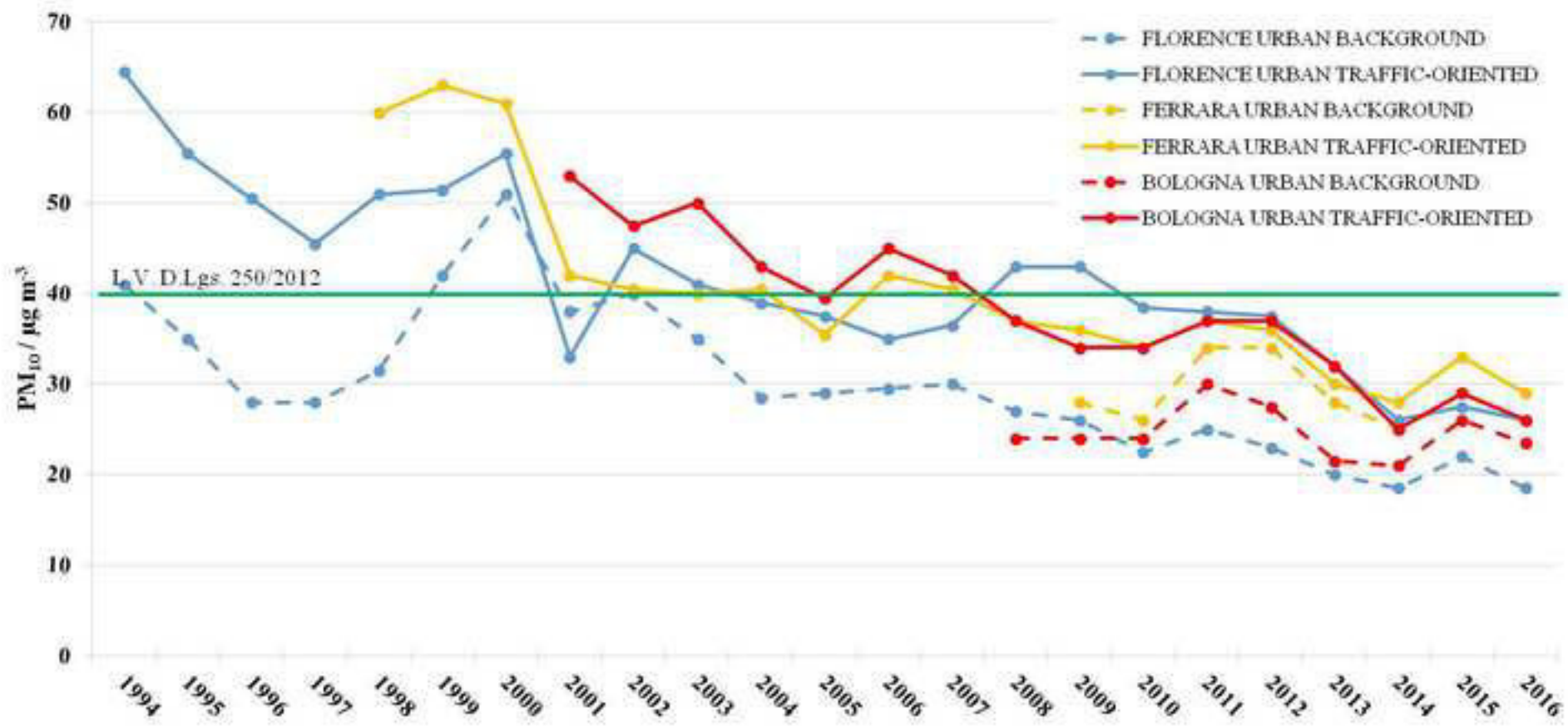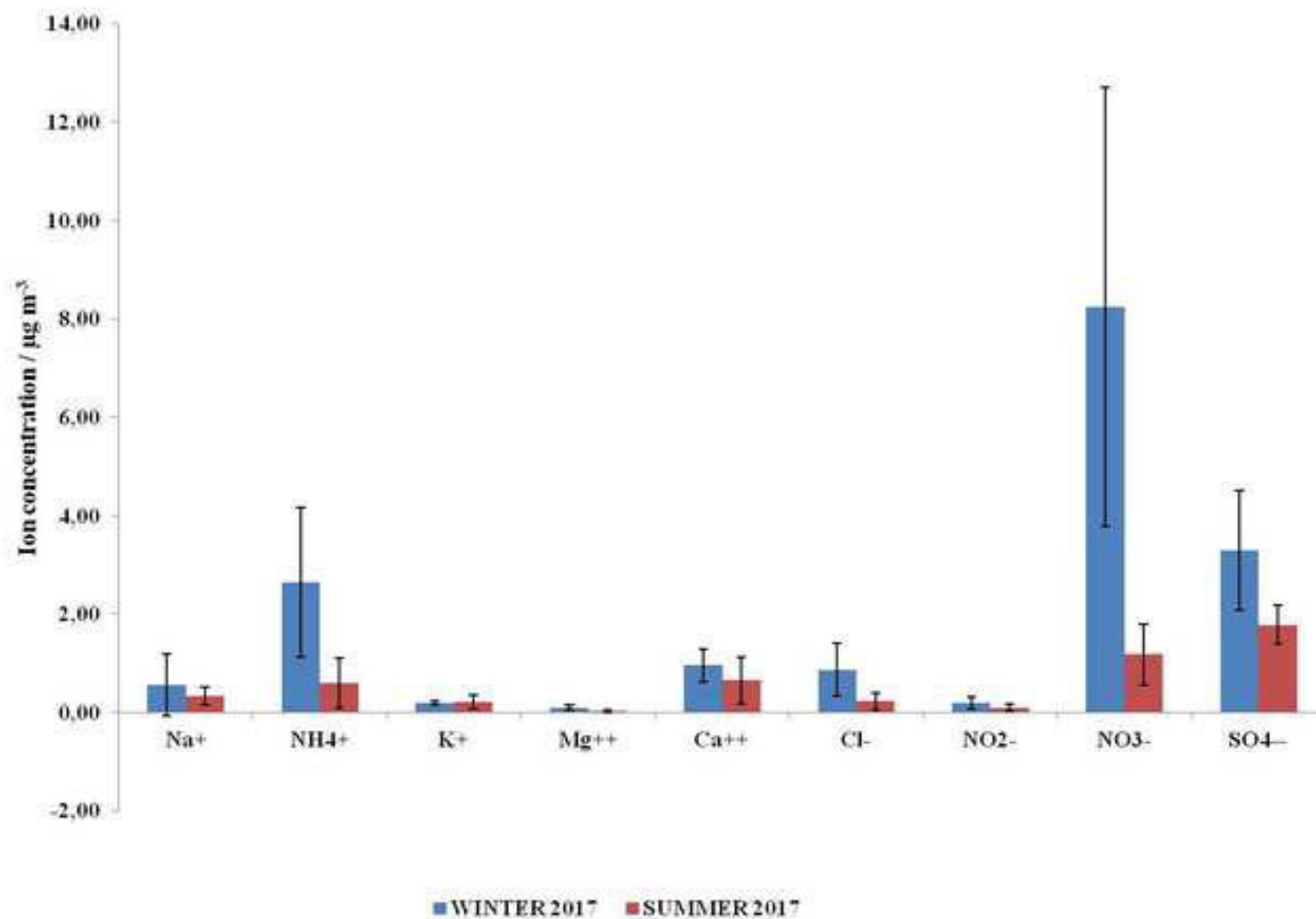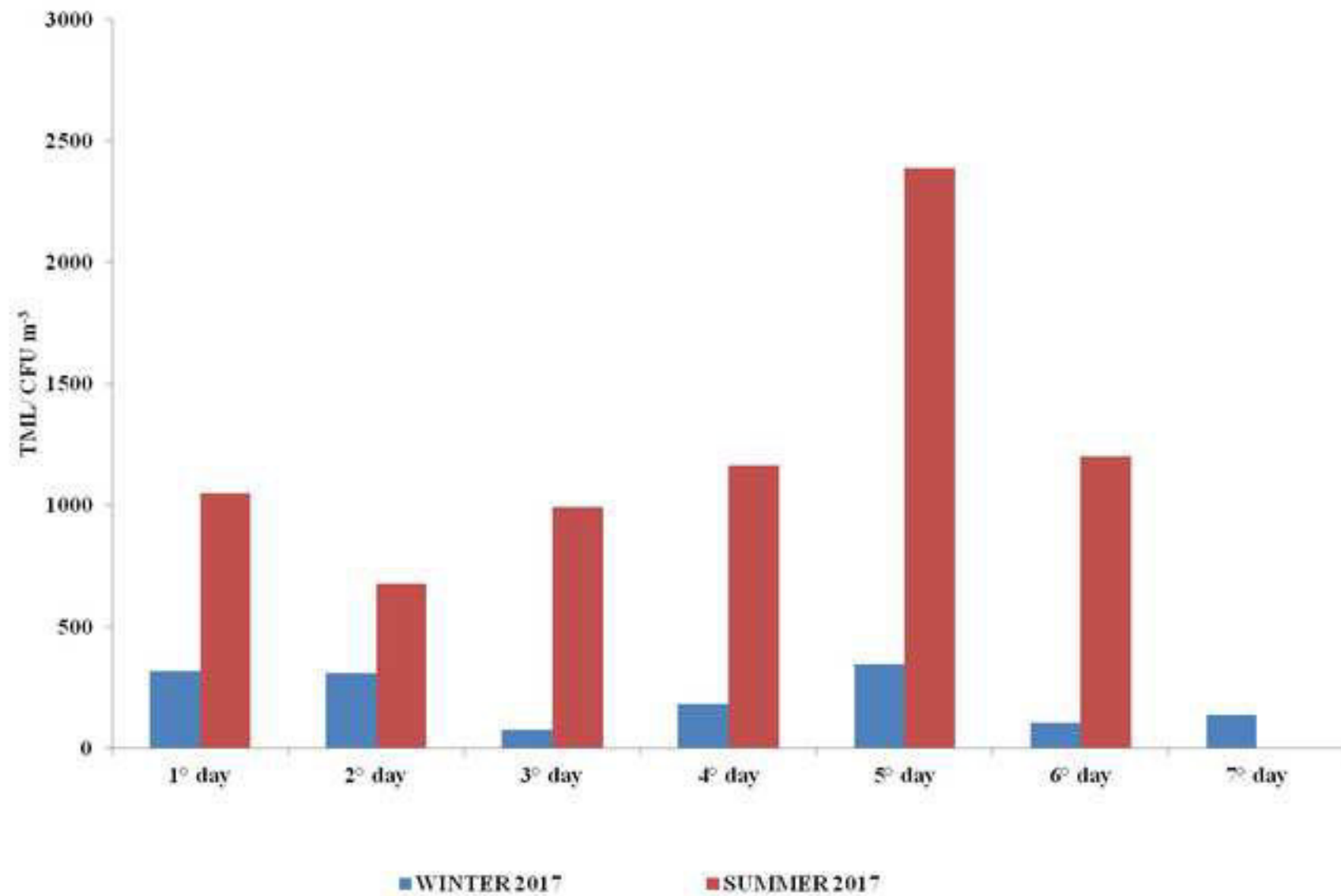
Table 1

	Urban traffic-oriented stations	Urban background stations
Bologna	• P.ta San Felice	• V. Chiarini
	• Fiera	• G. Margherita
Ferrara	• C. Isonzo	
	• C. San Giovanni	• Villa Fulvia
Florence	• Gramsci	• Boboli
	• Mosse	• Bassi

Table 2

Description of sampling sites	Bologna	Ferrara	Florence
Climate (Köppen classification)	Cfa	Cfa	Csa/Cfa
Mean annual temperature [°C]	13	13	15
Warmest month [°C]	Jul	Jul-Aug	Jul-Aug
Coldest month [°C]	Jan	Jan	Jan
Annual precipitation [mm]	709	634	912
Relative Humidity [%]	74	70	70
Metres above sea level [m]	54	9	50
Total area [km2]	141	405	102
Total population [capita] 01/01/2017 - Istat	388367	132009	382258
Population density [capita/km2]	2754	326	3747

Table 3

	Sampling period		Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	OC	EC
winter	Thu	9/02/2017	0.35	0.99	0.18	0.20	1.52	1.44	0.36	2.98	3.07	3.64	0.67
	Fri	10/02/2017	0.60	2.51	0.25	0.13	0.99	1.12	0.09	6.88	4.07	4.53	0.63
	Sat	11/02/2017	0.24	3.91	0.26	0.08	0.56	<LOD	<LOD	12.28	4.05	6.09	0.47
	Sun	12/02/2017	0.25	4.98	0.22	0.06	0.90	<LOD	<LOD	16.18	4.72	4.78	0.46
	Mon	13/02/2017	0.33	2.00	0.19	0.08	0.57	0.72	0.10	7.35	3.79	4.26	0.55
	Tue	14/02/2017	1.94	<LOD	0.14	0.08	1.10	<LOD	<LOD	5.76	2.14	3.82	0.53
	Wed	15/02/2017	0.15	1.49	0.15	0.09	1.05	0.19	0.21	6.27	1.29	4.51	0.64
summer	Tue	13/06/2017	0.53	<LOD	0.39	0.01	1.38	0.15	0.17	1.01	1.85	4.08	0.31
	Wed	14/06/2017	0.42	<LOD	0.26	0.01	0.81	0.12	0.08	1.38	1.82	3.32	0.26
	Thu	15/06/2017	0.42	<LOD	0.30	0.01	0.60	0.41	0.04	0.88	2.00	2.89	0.30
	Fri	16/06/2017	0.08	0.96	0.09	0.03	0.33	<LOD	<LOD	2.13	2.14	3.26	0.42
	Weekend	17-18/06/2017	0.20	0.24	0.03	0.07	0.14	<LOD	<LOD	0.51	1.11	2.35	0.23

Table 4

Sample name	ΔL*	Δa*	Δb*	ΔE*
BO_H_6m	-5.09±1.10	0.42±0.04	2.34±0.23	5.65±0.93
BO_H_12m	-5.69±1.42	0.62±0.15	4.02±0.78	7.00±1.59
BO_O_12m	-5.95±1.72	0.65±0.20	3.78±0.70	7.09±1.80
BO_V_12m	-0.20±0.91	0.12±0.03	0.08±0.05	0.67±0.58

Sample name	ΔL*	Δa*	Δb*	ΔE*
BO_H_6m	-5.09±1.10	0.42±0.04	2.34±0.23	5.65±0.93
BO_H_12m	-5.69±1.42	0.62±0.15	4.02±0.78	7.00±1.59
BO_O_12m	-5.95±1.72	0.65±0.20	3.78±0.70	7.09±1.80

Under Review Publication

POLLUTION EFFECTS ON STONES: A MULTIDISCIPLINARY APPROACH

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Abstract

It is generally agreed that air pollution represents an outstanding issue for the conservation of carbonate stone monuments and built heritage mainly in urban areas. Even if different studies focused on the effect of pollution on stone materials while others monitored air quality (gases and aerosol) of the environment surrounding specific cultural heritage, lack of knowledge still remains in the quantitative correlation between the concentration of particular atmospheric pollutants and their damage induced to stone.

In this regard, two-years long field exposure tests on model samples associated with particulate matter monitoring campaigns have been just concluded in Italian urban sites characterised by different environmental conditions, representing a non-invasive methodological approach to assess the impact of urban pollution on marble and limestone. After a general description of the adopted methodology, preliminary results of analyses performed on stone samples exposed in Ferrara are here presented and discussed, concentrating mainly on the aesthetical impact of soluble and carbon fractions of particulate matter on the selected lithotypes.

Introduction

Air pollution sill remains an outstanding problem not only for human health and preservation of the environment but also for the conservation of cultural heritage. In particular, monuments and built heritage located in urban sites are particularly affected by this issue as many concurrent emission sources (mainly vehicular traffic and heating systems) gather in a relative small area. Beside an irreversible loss of value of works of art, the decay of cultural heritage implies expansive conservation and restoration works. For these reasons, the study of factors and mechanisms involved in the decay of historic monuments and buildings is of primary importance to plan a preventive strategy.

In this regard, studies of pollution impact over the past few decades were mostly related to marble and limestone, widely employed everywhere as constructional and decorative materials, characterised by low porosity and chemical homogeneity (mainly composed by calcium carbonate) (Sabbioni 2003; Watt et al. 2009; Barca et al. 2014; Farkas et al. 2018). It is widely known that SO_2 reacts with carbonate stones to cause the formation of gypsum through sulphation process and that particulate matter, and in particular its carbonaceous fractions, has a driving role in soiling and black crusts formation. The black component of carbonaceous aerosol, also known as elemental carbon (EC) or soot and produced by incomplete combustion processes, is responsible for the dark colour of damage layer (Sabbioni 2003; Grossi and Brimblecombe 2004; Ghedini et al. 2006). Nevertheless, sulphation process, which became the dominant responsible of air pollution impact on stone at the end of the nineteenth century, has underwent a decrease because mitigations policies as well as use of low-S fuels have reduced the emissions of SO_2 in atmosphere from the mid-20th century (Grossi et al. 2008). Beside the ongoing drop of SO_2, higher concentration of NO_X and organic compounds deriving from vehicular traffic is detected in the majority of Western Europe cities. Therefore, a colour change of the damage layers from dark to greyish and brownish tones is increasingly observable on built heritage surfaces and it is expected to increase over time (Graber and Rudich 2006; Bonazza et al. 2007; Brimblecombe and Grossi 2007; Grossi 2016). Moreover, NO_x can interact with the stone substrate in the form of very soluble salts, generating microcracks due to significant changes of salts volume (Fermo et al. 2015).

Literature highlights that impact of air pollution on stone monuments has been mostly assessed by comprehensive analyses on specimens collected from historic built heritage to investigate the results of air pollution-stone interaction (Bonazza et al. 2005; Monna et al. 2008; Ruffolo et al. 2015; La Russa et al. 2017; Farkas et al. 2018) and by test in simulation chamber to better understand the role of different parameters with potential impact in deterioration phenomena and the related processes of damage in a simplified system (Rodriguez-Navarro and Sebastian 1996; Sabbioni et al. 1996; Chabas et al. 2015). Additionally, field exposure tests are gaining more relevance as they allow to study the ongoing environmental interactions on different materials in the same or different climate conditions (Realini et al. 1995; Zappia et al. 1998; Viles et al. 2002; Urosevic et al. 2012; Tidblad et al. 2012; Bonazza et al. 2013; Comite et al. 2017). In this context, atmospheric monitoring campaigns performed outdoor close to historic monuments provide further information about those gases and particles potentially dangerous for the conservation of the cultural heritage but they are still scarce (Nava et al. 2010; Ghedini et al. 2011).

The combination of field exposure tests of stone materials with simultaneous aerosol monitoring campaigns may have high potential for identifying the main emission sources in atmosphere in a specific site and gradually monitoring the related variations that happen on the exposed built materials. This approach would contribute to develop damage and dose-response functions useful to quantify the effect of pollution on cultural heritage and thus plan long-term strategies for built heritage management. In this regard, the Institute of Atmospheric Sciences and Climate of the National Research Council of Italy (ISAC-CNR, Bologna) and the Department of Physics and Earth Sciences of the University of Ferrara are collaborating to study the impact of urban atmospheric pollution on carbonate stones by performing field exposure tests for 24 months in Italian cities characterised by different environmental conditions (i.e. Bologna, Ferrara and Florence). The doctorate research intends to monitor over time and quantify (in terms of soluble and carbon fractions) the material accumulated on the exposed surface of stone samples in order find a possible interaction with colorimetric and chemical changes of stones. In particular, chemical components of deposited material was analysed for assessing the mass of soluble and carbon fractions per surface unit of stone specimen. Further information would be collected by weekly monitoring campaigns of particulate matter performed every 6 months close to the selected sites for correlating the soluble and carbon fractions present into atmosphere with those fractions detected on stone surface and potentially dangerous for its conservation.

Beside a general description of the methodological approach selected for the whole doctorate research, this paper focus on presentation and discussion of results obtained from analyses performed on material deposited on stone samples exposed in Ferrara over time. Particular attention is here paid to quantify of soluble and carbon fractions of particulate matter deposited over time on the selected lithotypes and to identify a link among these fractions and variation of surface colorimetric parameters.

Materials and method
Field exposure programme
Carrara Marble (CM) and Verona Red Marble (VRM) were selected as reference materials because of their homogeneous chemical composition (mostly calcium carbonate) and as they have been widely used in monuments and built heritage throughout the world. CM is a medium-fine grained pearly white to light grey metamorphic stone extracted in Apuan Alps (Tuscany) while VRM is a nodular rose limestone with several red stylolitic joints and calcite veins. In particular, the lower stratigraphic unit of the Rosso Ammonitico Veronese formation, extracted from Valpolicella area (Veneto) and called Nembro Limestone, was chosen for this research for its higher colour homogeneity and the absence of macrofossil. Samples were first polished and prepared as tablets of 12 x 12 x 2 cm. CM was exposed in Bologna, Ferrara and Florence to assess the performance of the same lithotype in different environmental conditions while VRM stood beside the marble only in Ferrara to compare the response of different stones to the same environmental parameters. Samples were exposed outdoor, partially sheltered by direct rain-wash, on specifically built galvanised metallic racks

able to host specimens in diverse orientation (horizontal, 45°-oblique and vertical) to evaluate how positioning may influence particulate matter deposition and removal by wind-driven precipitations. Particularly, specimens were arranged in order to take a whole sample every 6 months to analyse the carbon fractions of material deposited on the exposed surface and another one for soluble ions assessment. Moreover, two samples were designed for colorimetric analysis and other two ones, dedicated for further analyses, remained exposed for the complete period. Racks were exposed in urban areas characterised by pollution due to vehicular traffic: i) a first-floor terrace of the National Research Council of Italy (CNR) in Bologna, ii) a roof terrace of Turchi di Bagno Palace in Ferrara and iii) a loggia of San Marco Museum in the centre of Florence. The experimental tests started in June/July 2016 and lasted for 24 months. Simultaneously, 10 quartz fibre filters were exposed horizontally in each site for 2 years for monitoring atmospheric particulate matter every 6 months (in terms of soluble and carbon fractions). Additionally, particulate matter (PM) monitoring campaigns were planned close to the exposure racks every 6 months in order to monitor the surrounding atmospheric composition (soluble and carbon fractions) and correlate the results with the material actually deposited on stone surface.

Exposed surface of samples periodically (i.e. every 6 months) underwent Colorimetric Analyses as well as Ion Chromatography and Elemental Analysis-Isotope Ratio Mass Spectrometry of carbon were performed on the material accumulated on it in order to assess the state of deterioration of the stone surface. The results of these last analyses are compared with soluble ions and carbon fractions detected every 6 months during weekly aerosol monitoring campaigns performed in each site and with those measured on quartz fibre filters passively exposed. Furthermore, the assessment of deposited particulate matter and its interaction with stone substrate would be further investigated at the end of 2 years of exposure with Scanning Electron Microscopy equipped with Energy Dispersive X-Rays Spectroscopy and Inductively Coupled Plasma Mass Spectrometry of the deposited material. These analyses are still under execution.

Characterisation of exposure site: Ferrara

Ferrara (44°50′7.07″ N, 11°37′11.51″ E; 9 m above sea level) is an historic city of roughly 132000 inhabitants located in Emilia-Romagna region. For its beauty and cultural relevance, it has been nominated as UNESCO World Heritage Site. Ferrara is characterised by a warm damp temperate climate with hot summer (Cfa) (Rubel et al. 2017), with temperature between 0°C and 32°C and annual mean precipitation around 634 mm. Even if Ferrara is not so much rainy, high relative humidity is distinctive of this area as fog in autumn and winter or muggy weather during summer.

Ferrara is located in Po Valley, one of the most polluted areas of Italy. Industry, present in many facilities especially as chemical plants, constitutes one of the main source of pollution in Ferrara municipality beside vehicular traffic (as local road network and a motorway located rather close to the city centre), heating systems and agricultural practices (mostly farming) developed in the city and surroundings (Gerdol et al. 2014). Furthermore, the topography of Po Valley, surrounded by Alps and Apennines mountain chains, favours air stagnation and reduced pollutant dispersal both in warm seasons, with high level of photochemical smog, and in cold months, characterised by significant level of PM concentrations. Nevertheless, mean yearly concentration of pollutants measured by the local environmental agency in urban traffic, background and industrial stations in 2017 were within limit value fixed by Legislative Decree no. 250/2012 for human health protection: NO_2 (30 µg m^{-3} yearly average, 40 µg m^{-3} legal limit); PM_{10} (33 µg m^{-3} yearly average; 40 µg m^{-3} legal limit); $PM_{2.5}$ (23 µg m^{-3} yearly average; 25 µg m^{-3} legal limit); CO (<0.6 mg m^{-3} yearly average, 10 mg m^{-3} legal limit); SO_2 (<14 µg m^{-3} yearly average, 20 µg m^{-3} legal limit) (Arpae Emilia Romagna - sez. Ferrara 2017).

The area selected for the exposure tests was located in the city centre at Palazzo Turchi di Bagno (Corso Ercole I d'Este, 32), on the side of the palace oriented towards the rather busy Via Porta Mare (Fig. 1A). Palazzo Turchi di Bagno, located in front of the illustrious Palazzo dei Diamanti, is a Renaissance architectural work designed by Ar. Biagio Rossetti. The other sides of the Palace overlook a botanic garden and a restricted traffic

area. In a straight line, train station, Petrochemical area of Ferrara and highway A13 are respectively 1.4 km, 3.0 km and 4.4 km far from the building.

50 samples of Carrara Marble and 50 of Verona Red Marble were exposed on the roof terrace at the first floor of the Palace (around 6 m from the ground level) but other 9 stone samples (5 of CM and 4 of VRM) were arranged obliquely in the same building in a windowsill of the Museum of Palaeontology and Prehistory P. Leonardi, facing Corso Porta Mare (Fig. 1B).
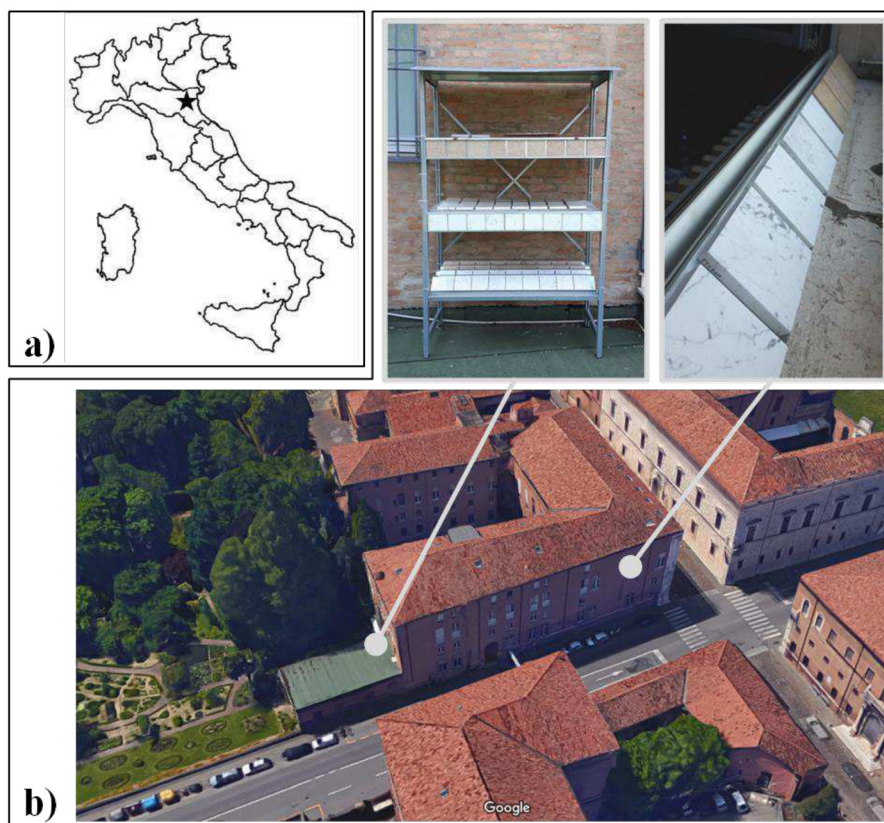
Fig. 1 a) Geographic location of the study area in Italy. b) Location of racks hosting stone samples at Palazzo Turchi di Bagno

Analytical methodologies

Colorimetric features of the exposed surface of stone specimens were analysed every 6 months and compared with colorimetric parameters of both lithotypes before exposure. Surface of the designed sample was divided in 4 quarters so as to assess colour on only one quarter every 6 months, repeating the analysis 5 times in 5 different points. This measure was performed by a portable spectrophotometer Konica Minolta CM-700d to measure CIEL*a*b* coordinates for the definition of luminosity (L*), red-green component (a*), blue-yellow component (b*) and total colour difference (ΔE*), according to UNI 15886:2010. The spectrophotometer has a measurement geometry of d/8° with a xenon light source with UV cut filter, a silicon photodiodes array detector and a target mask with 8 mm of diameter. Colour data are assessed for the D65 illuminant, with the observer at 10°, including the specular component of light. The colorimetric analysis was carried out on horizontal samples of both lithotypes after 6, 12, 18 and 24 months as well as on oblique and vertical marble and limestone samples after 12, 18 and 24 months.

The assessment of carbon fractions present in the material accumulated on stone samples is useful for discriminating the possible emission sources of carbon present into atmosphere. Total carbon (TC) is composed by carbonate carbon (CC), ascribable mainly to stone substrate or soil dust, and non-carbonate carbon (NCC). The NCC fraction is in turn made by elemental carbon (EC), predominantly a consequence of combustion processes, and organic carbon (OC) from primary and secondary both natural and anthropogenic sources

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(Ghedini et al. 2006). In this regard, the material deposited on the exposed surface of a whole sample was mechanically removed with a stainless steel spatula every 6 months from specimens with different orientation, whenever a suitable amount of particulate accumulated on the surface. A new method to measure carbon fractions was purposely set up refining the analytical approaches tested by Ghedini et al. (2006), Natali and Bianchini (2015) and Natali et al. (2018) and described in Vidorni (2019). It involves the use of an automated elemental analyser coupled with isotope ratio mass spectrometry (EA-IRMS) and a muffle furnace. In this case, an Elementar Vario Micro Cube EA in line with an ISOPRIME 100 IRMS operating in continuous flow mode was used. This method is based on thermally-based separation (TBS) that exploits the distinct temperature stabilities of the different carbon fractions. In addition, isotope ratio mass spectrometry represents a further tool to complement the TSB method and allows the validation of the carbon pool delineation. The ratio of stable carbon isotopes ^{13}C and ^{12}C ($\delta^{13}C$) provides information about natural and anthropogenic sources of carbon and it is obtained as:

$$\delta^{13}C = 1000 \cdot [(^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{standard}) / {}^{13}C/^{12}C_{standard}]$$

based on the international Vienna Pee Dee Belemnite (V-PDB) isotope standard. Considering that these samples have a carbon content around 12-15 %, the minimum amount of specimen needed for an exhaustive investigation of TC and its isotopic ratio is between 0.8 mg and 1 mg. The analysis of samples exposed for 24 months is still in execution.

A sample of both lithotypes was collected every 6 months to detect water-soluble ions present on its whole exposed surface. The sample surface was first washed with deionised and purified water (Milli-Q by Millipore Corporation) and the total soluble fraction was extracted in 100 mL of pure water. An aliquot of solution was filtered with pre-cleaned syringe filter (Polytetrafluoroethylene –PTFE–membranes) to remove particulates with a diameter higher than 0.45 µm from the sample. Water-soluble ions were analysed by an ICS-2000 Thermo Fischer Ion Chromatograph (Dionex, California, USA). Anions (Cl^-, NO_3^-, SO_4^{2-}) assessment was carried out by means of IonPac™ AS11 column utilising KOH as eluent while cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were detected with IonPac™ CS16 column and methylsulfonic acid (MSA) as eluent.

__Results and discussions__

Carrara Marble analysed before exposure is characterised by a pronounced lightness (mean value: 89.60) and weak chromaticity coordinates (mean values of a* and b*, respectively: -0.46 and 0.14). On the contrary, Verona Red Marble has a hue that results from the combination of red (mean a*: 7.27) and yellow (mean b*: 16.65) components while lightness is lower than that of CM (mean L*: 67.29).

The exposure outdoor of samples in a condition that favours the deposition of particulate matter and prevents its removal by rain washout led to different variations of total colour depending on sample orientation and lithotype (Fig. 2). Concentrating upon CM, horizontal specimens displayed a gradual increasing ΔE* trend over time (passing from 10.88 ± 1.39 after 6 months of exposure to 20.78 ± 1.46 after 24 months), much higher than that detected on oblique samples (from 2.44 ± 1.21 after 12 months and 15.98 ± 2.59 after 24 months of exposure). On the contrary, vertical marble specimens underwent a lower change of total colour, remaining rather constant over time around 1.19 ± 0.32. ΔE* measured on horizontal limestone samples, by contrast, remained always below values assessed on marble specimens, reaching the lowest value after 12 months of exposure (2.91 ± 1.51) and the highest one after 18 months (7.74 ± 0.81). ΔE* of oblique and vertical limestone samples remained rather constant over time, with very similar values: the average value of all points analysed on oblique samples (3.89 ± 1.14) were comparable to those detected on vertical ones (3.60 ± 1.17). Comparing with marble, vertical limestone specimens underwent always a higher ΔE* while in general oblique limestone samples showed a variation of total colour lower than the equivalent one of marble.
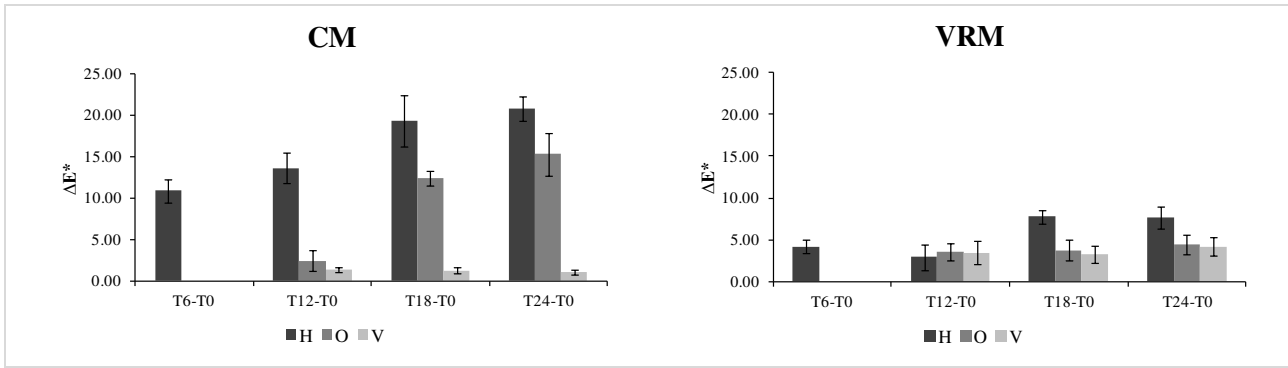
Fig. 2 Mean variation of total colour appearance (ΔE*) of Carrara Marble (CM) and Verona Red Marble (VRM) samples exposed in Ferrara for 6, 12, 18 and 24 months compared with samples before exposure. H, O and V stand for horizontal, oblique and vertical samples, respectively

In particular, the variation of total colour in marble can be ascribable to a noticeable blackening effect ($\Delta L^* < 0$), with exception of vertical samples that underwent a slight whitening effect ($\Delta L^* > 0$), and a shift toward the yellow component ($\Delta b^* > 0$) over time, as highlighted also in Fig.3. The darkening effect combined with a yellowing appearance is more evident in horizontal and oblique marble samples and intensified over time. The variation of red-green component remained always negligible in all marble samples. Conversely, colour changes of limestone samples are characterised by a slight shift toward the green component ($\Delta a^* < 0$) independently from orientation, a small change toward blue factor ($\Delta b^* < 0$) in horizontal and vertical samples and a general blackening effect ($\Delta L^* < 0$) in horizontal and oblique specimens but a slight whitening effect ($\Delta L^* > 0$) in the vertical ones. VRM before exposure is indeed characterised by a colour appearance more complex and variable than CM and this can influence the colorimetric analysis.
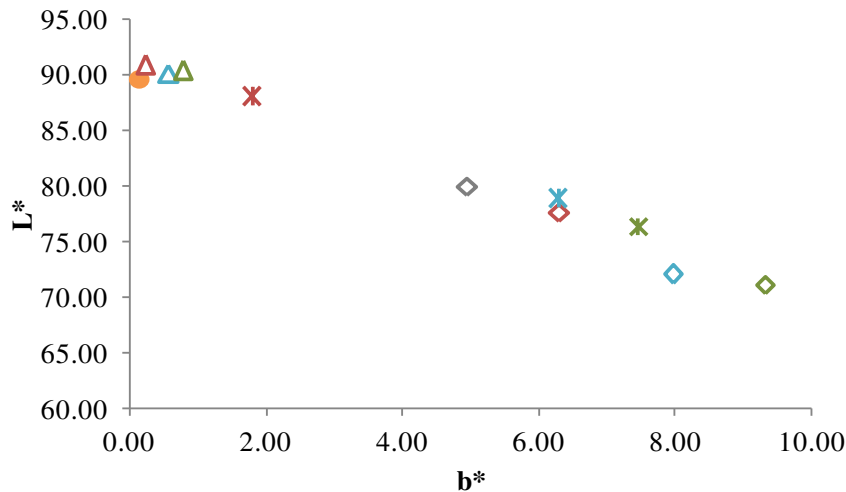

Fig. 3 Lightness (L*) versus blue-yellow component (b*) measured on surface of Carrara Marble horizontal (rhombus), oblique (star), vertical (triangle) samples exposed in Ferrara over time. Orange dot represents mean values of marble before exposure while grey, red, light-blue and green markers stand for samples exposed respectively for 6, 12, 18 and 24 months

The elemental analyser coupled with isotope ratio mass spectrometry provided the identification and quantification of carbon fractions as percentage calculated over mass of the analysed sample portion. However, it was considered more appropriate to report here the data as mass of carbon fractions detected on the whole material collected from the sample divided by the exposed surface of stone specimen (144 cm^{-2}), indicated as C$_{surface}$.

Figure 4 shows $TC_{surface}$ of horizontal and oblique samples of both lithotypes measured after 6, 12 and 18 months of exposure. Material deposited on all vertical samples for the whole considered period as well as on oblique sample after 6 months of exposure did not reached the minimum amount necessary for TC analysis (i.e. 1 mg). $TC_{surface}$ of horizontal Carrara Marble samples (between 33.30 µg cm^{-2} and 118.35 µg cm^{-2}) remained always higher than that detected on limestone specimens (from 23.54 µg cm^{-2} and 71.14 µg cm^{-2}) throughout the analysed period. Concentrating upon oblique specimens, $TC_{surface}$ was similar for both lithotypes after 12 months of exposure (mean value around 45.45 µg cm^{-2}) while it revealed slightly higher value on marble sample after 18 of exposure (85.10 µg cm^{-2} for CM and 66.49 µg cm^{-2} for VRM). Nevertheless, both lithotypes showed an increasing trend over time both for horizontal and oblique specimens but with higher values on horizontal samples.
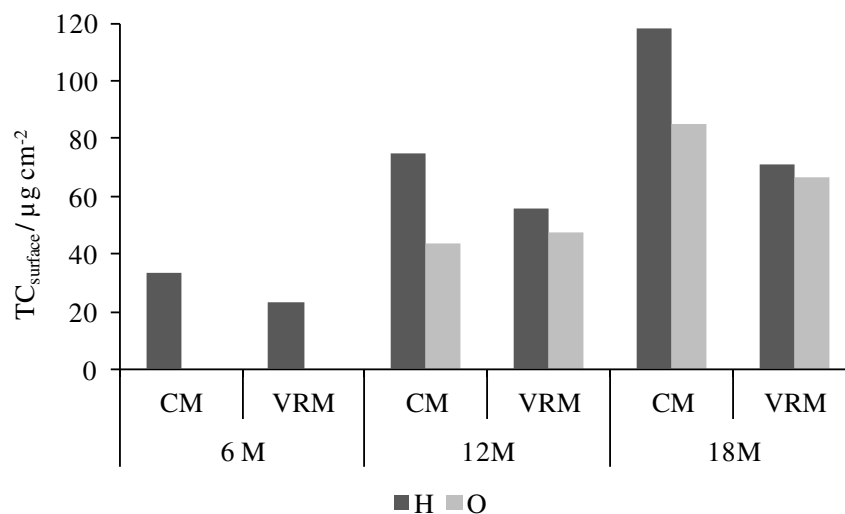

Fig. 4 TC amount per surface area (TC_surface) measured on the material collected from the exposed surface of CM and VRM samples horizontally and obliquely exposed in Ferrara for 6, 12 and 18 months

The percentage of each carbon fraction respect to TC highlights that NCC always prevails over CC for both Carrara Marble and Verona Red Marble samples horizontally and obliquely exposed (Tab. 1). In this regard, NCC was always predominantly composed by OC while EC represented the lowest portion. However, it was not possible to evaluate OC and EC of limestone after 6 months of exposure because the amount of deposited mater was sufficient only for TC and CC measurement. Considering horizontal samples, OC ranged between 54 % and 72 % for marble samples and between 54 % and 80 % for limestone ones while EC remained between 7 % and 21 % for CM and between 0 % and 30 % for VRM, thus highlighting a more intense variation of carbon fractions on limestone over time. Oblique samples experienced higher accumulation of OC on limestone samples respect to the corresponding marble specimen of the same exposure period, always remaining by far higher than EC, ranging in general between 2 % and 18 %. The prevalence of OC over EC confirms the predominance of organic fraction detected also in atmosphere during monitoring campaigns of particulate matter carried out in Ferrara area between 2010 and 2012 by Perrino et al. (2014) as well as the tendency of higher OC values measured on more recent damage layers or in those collected from monument sides exposed directly to air pollution due to traffic (Bonazza et al., 2005).

Comparing lightness (L*) with the detected amount of EC per surface unit ($EC_{surface}$) of marble samples (Fig. 5a), it is clear that increasing values of $EC_{surface}$ detected over time were related to a darkening effect of stone surface, more evident on horizontal samples that on oblique ones. This is typical of the darkening process as described for damage layers in Brimblecombe and Grossi (2004) and Bonazza et al. (2007). Moreover, a shift towards more yellow component over time was detected on both horizontal and oblique specimens in

conjunction with an increase of $OC_{surface}$, as highlighted in Fig. 5b. This suggest that the gradual deposition of OC component is responsible for the yellowing effect observable over time on the surface of CM samples.
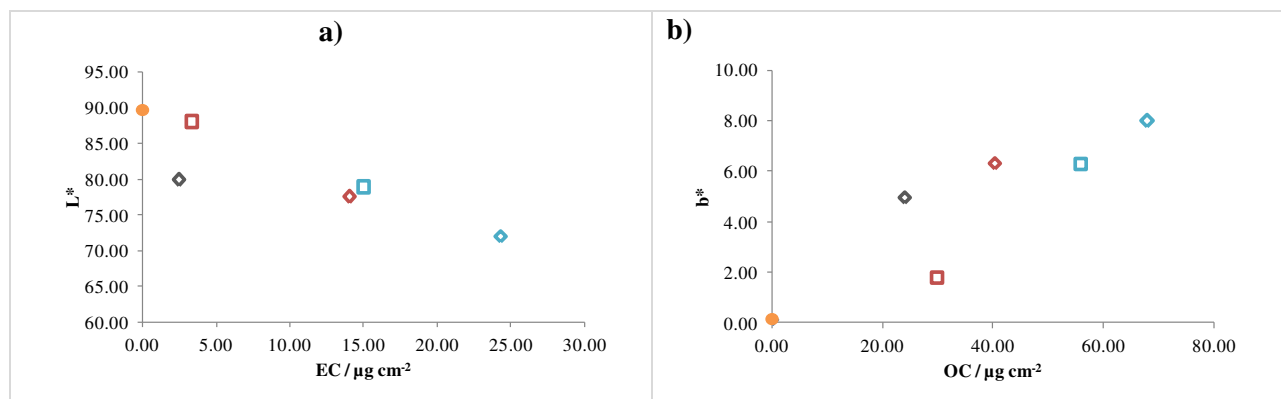

Fig. 5 Lightness versus $EC_{surface}$ (a) and blue-yellow component versus $OC_{surface}$ (b) measured on surface of Carrara Marble horizontal (rhombus) and oblique (squares) samples exposed in Ferrara over time. Orange dot represents mean values of marble before exposure while grey, red and light-blue markers stand for samples exposed respectively for 6, 12 and 18 months

Comparing the isotopic ratio assessed on horizontal samples at different exposure time (Table 1), both lithotypes showed similar value of $\delta^{13}C_{TC}$ over time, slightly more positive in CM samples (mean value: -19.5 ‰) than in VRM ones (average: -21.0 ‰). $\delta^{13}C_{CC}$ remained constant around 0.0 ‰ over time for both lithotypes as well as the mean value of $\delta^{13}C_{OC}$ measured for marble and limestone samples was always -25.1 ‰. On the contrary, $\delta^{13}C_{EC}$ underwent the highest variations among the different kind of stone, showing more positive mean values on limestone specimens (-14.1 ‰) than on marble ones (-27.1 ‰), and over time as it underwent a general variation toward more positive values after 18 months of exposure. Also material deposited on oblique specimens of both lithotypes displayed values of $\delta^{13}C_{TC}$, $\delta^{13}C_{CC}$ and $\delta^{13}C_{OC}$ similar to those measured on horizontal samples. However, different values of $\delta^{13}C_{EC}$ were detected on oblique samples, reaching more positive values on marble samples (-19.6 ‰) than on limestone ones (-24.2 ‰), contrary to what was measured in horizontal samples.

	Sample	CC %	OC %	EC %	$\delta^{13}C_{TC}$ ‰	$\delta^{13}C_{CC}$ ‰	$\delta^{13}C_{OC}$ ‰	$\delta^{13}C_{EC}$ ‰
6 M	CM_H	21	72	7	-20.2	-0.7	-24.8	-29.5
	VRM_H	20	n.a	n.a	-21.1	-0.5	n.a	n.a
12M	CM_H	27	54	19	-18.3	1.0	-24.5	-28.5
	CM_O	24	69	8	-19.0	0.3	-25.2	-22.7
	VRM_H	16	54	30	-21.7	-1.1	-24.4	-28.1
	VRM_O	14	75	10	-21.7	-0.9	-25.1	-25.7
18M	CM_H	22	57	21	-20.0	-1.1	-26.0	-23.4
	CM_O	17	66	18	-19.9	0.4	-25.9	-16.6
	VRM_H	20	80	0	-20.1	-0.4	-25.9	0.0
	VRM_O	21	77	2	-20.6	-0.6	-26.0	-22.6

Table 1 CC, OC and EC calculated as percentages of TC and isotopic ratio of TC, CC, OC and EC of Carrara Marble and Verona Red Marble horizontally and obliquely exposed in Ferrara for 6, 12 and 18 months

Relative proportion of stable carbon isotopes is different in each carbon reservoirs and thus it can provide useful information about the sources of particulate matter accumulated on stone samples. $\delta^{13}C_{TC}$ is not so distinctive of a specific source as it results from the combination of the isotopic ratio of all carbon fractions. For that reason, it is really important to assess the $\delta^{13}C$ and the concentration of each carbon fraction to evaluate the main emission sources. Value of $\delta^{13}C_{CC}$ acquired on all analysed specimens is characteristic of carbonate stones. This can have two different sources: one related to the deposited soil dust and the other associated to the weathered stone substrate. In this context, the constant concentration of CC/TC over the whole exposure time suggests the deposited atmospheric soil dust as more reliable source of the carbonate component. Focusing on OC, its isotopic ratio remained always around -25.3 ± 0.7 ‰ for all samples, highlighting a constant source over time. However, this value pertains to unleaded gasoline emissions (Widory 2006) as well as to C3-plants released directly as biogenic components or from wood combustion. Furthermore, also degradation processes of the organic component of particulate matter can affect its isotopic ratio. In this regard, compounds derived from oxidation processes are generally depleted in heavier isotopes (Martinsson et al. 2017 and related references) while photochemical aging of organic aerosol leads to a loss of organic carbon from the particles and thus to a gradual enrichment in ^{13}C of the remaining aerosol phase (Mašalaitė et al. 2017). Finally, $\delta^{13}C_{EC}$ remained in general between -29.5 ‰ and -16.6 ‰ over time. It is known that combustion processes are responsible of EC emissions and the isotopic ratio generated through different fossil combustion ranges from –26 to –20 ‰ for gasoline, –28 to –24 ‰ for diesel, –27 to –23 ‰ for natural gas (methane) and –25 to –21‰ for coal (Martinsson et al. 2017). Therefore, EC derives from anthropogenic combustion processes but the relatively wide range of detected $\delta^{13}C_{EC}$ makes difficult the identification of the specific fossil fuel.

Ion chromatography results related to horizontal samples shows in general a prevalence of Cl^- over NO_3^- and SO_4^{2-} in both kind of stones during each analysed period, with exception of Carrara Marble samples after 24 months of exposure where SO_4^{2-} reached concentration similar to Cl^- (Fig. 6a). Comparing the concentration of Cl^- per surface unit found on both lithotypes during each analysed period, it remained between 4.36 µg cm^{-2} and 21.97 µg cm^{-2} for CM and from 1.07 µg cm^{-2} to 31.28 µg cm^{-2} for VRM, with higher values on VRM after 12 and 18 months of exposure while slightly more abundant in CM after 6 and 24 months of exposure. NO_3^- maintained similar values for marble and limestone samples during each period with values in general between 3.01 µg cm^{-2} and 11.10 µg cm^{-2} in CM and from 1.69 µg cm^{-2} to 11.83 µg cm^{-2} in VRM. On the contrary, it is interesting to observe that SO_4^{2-} (in general from 4.38 µg cm^{-2} to 13.18 µg cm^{-2} in CM and between 2.05 µg cm^{-2} and 4.54 µg cm^{-2} in VRM) measured on the marble was double that detected on VRM during the considered periods, reaching even 5 times higher concentration after 18 months of exposure.

Concentrating upon cations, Na^+ prevailed over the other cations within 18 months of exposure for both CM (with values between 11.43 µg cm^{-2} and 16.51 µg cm^{-2}) and VRM (13.58 µg cm^{-2} and 15.14 µg cm^{-2}) samples while it markedly decreased after 24 months of exposure for both lithotypes (2.34 µg cm^{-2} for CM and 0.76 µg cm^{-2} for VRM) (Fig.6b). Also Ca^{2+} was generally rather abundant in both kind of samples reaching higher values than other cations after 24 months of exposure (7.94 µg cm^{-2} in CM and 7.69 µg cm^{-2} in VRM), with exception after 12 months of exposure that reached values below limit of detection. Mg^{2+} remained constant within 18 months of exposure and similar in both lithotypes around 4.01 ± 0.41 µg cm^{-2} while it became negligible after 24 months of exposure. In general, K^+ and NH_4^+ displayed always values very low.

Ions concentration of oblique samples exposed for 6 months is not available while after 24 months of exposure both samples exposed on the roof terrace as well as those placed on Museum windowsill were analysed (Fig. 6c-d). Anions concentrations per surface unit of oblique CM and VRM over time showed a similar trend to those detected on the same kind of specimens horizontally exposed but generally with lower values, with the prevalence of Cl^- over NO_3^- and SO_4^{2-} after 12 and 18 months of exposure while in general SO_4^{2-} was the predominant anion after 24 months of exposure. Furthermore, also cations maintained a trend similar to that detected on horizontal specimens, as Na^+ prevailed after 12 and 18 months while Ca^{2+} after 24 months of exposure, reaching till 14.84 µg cm^{-2}. The amount of K^+ and NH_4^+ was negligible also in oblique samples while

Mg^{2+} concentration remained similar to the mean value assessed on horizontal samples both on CM and VRM after 12 and 18 months of exposure and underwent an evident reduction after 24 months of exposure. Moreover, considering the two location of exposure, samples located on roof terrace revealed higher concentration of ions than those exposed on windowsill mainly for CM (Fig. 6c-d).
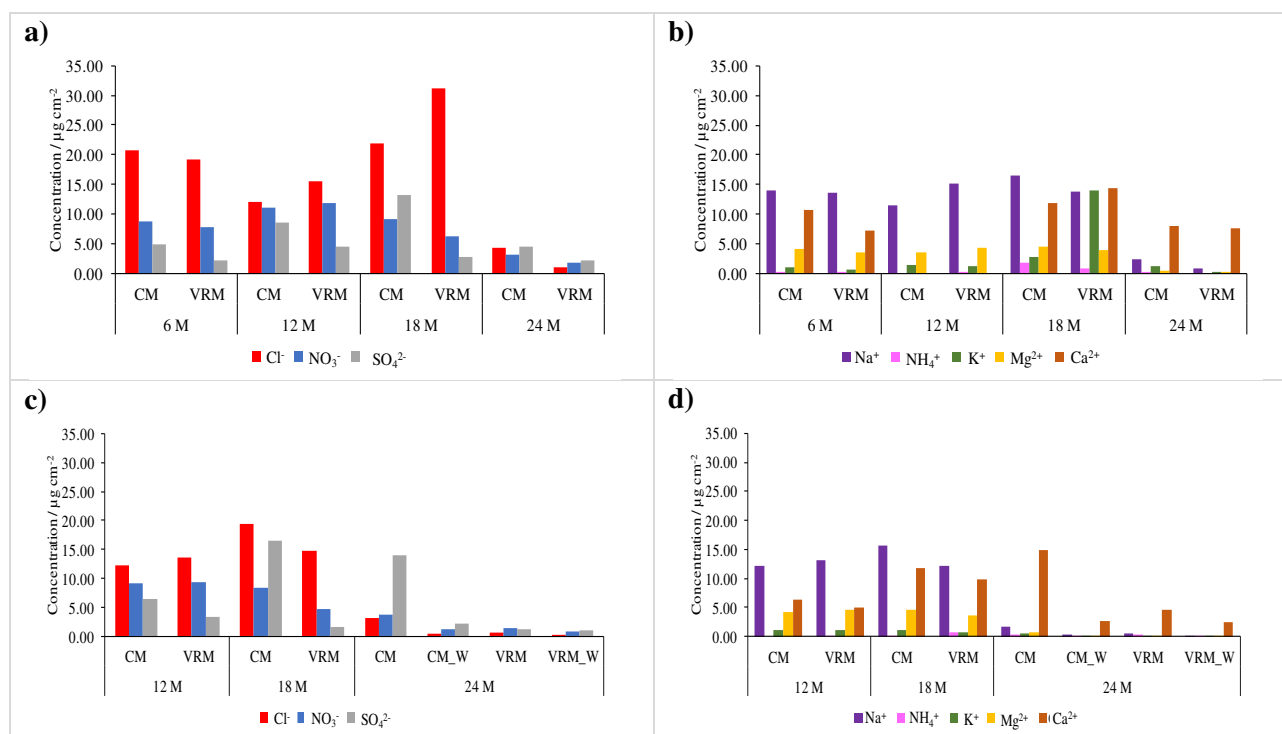

Fig. 6 Concentration of anions (a, c) and cations (b, d) per surface area measured on the exposed surface of Carrara Marble and Verona Red Marble samples horizontally (a, b) and obliquely (c, d) exposed in Ferrara for 6, 12, 18 and 24 months

In contrast, ion amount detected on samples vertically exposed for 24 months resulted very low independently from the kind of stone. In particular, small concentration of SO$_4^{2-}$ (5.11 µg cm^{-2} in CM and 5.65 µg cm^{-2} in VRM) and Ca^{2+} (3.98 µg cm^{-2} in CM and 4.71 µg cm^{-2} in VRM) were detected on both lithotypes, suggesting the possible presence of underway sulphation process.

Conclusions

Atmospheric particulate matter in urban sites represents a hazard for stone surfaces since it can deposit and interact with stone substrate leading to aesthetical variations and chemical interactions. Field exposure tests combined with atmospheric PM monitoring campaigns were selected as methodological approach for assessing the effect of atmospheric pollution on carbonate stone substrates in different environmental sites. In this study, we present and discuss results about the colorimetric changes of lithotypes surface and the amount of soluble and carbon fractions detected on the material deposited on stone specimens exposed in Ferrara.

Considerable change of total colour (ΔE*) with increasing amount over exposure time was observed mainly on the analysed surface of Carrara Marble samples, affecting principally those horizontally and obliquely placed. This ΔE* was mostly related to a blackening effect (ΔL*<0) and a shift toward the yellow component (Δb*>0) that became more evident over time. In this regard, the comparison of colorimetric results with carbon fractions amount per surface unit measured on CM samples highlights that the blackening effect was induced by the increasing EC concentration accumulated on stone surface over time while the observed yellowing effect was related to the gradual deposition of OC on stone surface over time. A variation of total colour was detected also on VRM horizontal samples, in general with a slightly increasing trend over time, but with lower

amount respect to CM specimens while ΔE* of oblique and vertical limestone samples were limited and stable over time.

Both CM and VRM samples underwent a growing accumulation of TC on samples surface over time, more on horizontal samples than on oblique ones. In general, CC was always detected in lower concentration respect to NCC in all analysed specimens. The related $\delta^{13}C_{CC}$, constant around 0.0 ‰ over time for both lithotypes, is characteristic of carbonate stone and the stable concentration of CC/TC over time suggest the accumulation of fragments of carbonate stone in the form of soil dust while it rules out the possible provenance of the carbonate component from weathered marble and limestone substrate as results of outdoor exposure. Among NCC components, OC prevailed over EC in both lithotypes independently from exposure orientation, in accordance to the general tendency of predominant OC concentration detected in atmospheric PM of Ferrara (Perrino et al. 2014) and in recent damage layers (Bonazza et al. 2005). Ratio of stable carbon isotopes of each carbon fraction allows useful information about the sources of particulate matter accumulated on stone samples. The stability over time of $\delta^{13}C_{OC}$, around -25.3 ‰ in all material deposited on stone samples, implies a source of OC not subjected to seasonal changes but constant over time. As a consequence, traffic emissions appear to be the most likely among possible OC origins. Furthermore, $\delta^{13}C_{EC}$ allows to state the origin of EC from anthropogenic combustion processes but its relatively wide range (between -29.5 ‰ and -16.6 ‰ over time) makes difficult the identification of the specific fossil fuel.

Concentrating upon ions, there is a good relation between the amount per surface unit of Cl^- and Na^+ on both horizontal and oblique lithotypes within 18 months of exposure, which may be related to sea-salt spray and marginally to de-icing salt. Also SO_4^{2-} and Ca^{2+} were rather abundant on the analysed samples over time (with higher values on CM than on VRM) and they become the dominant ions after 24 months of exposure, indicating a probable ongoing sulphation process.

Further analyses are currently underway in order to examine the state of conservation of stone surface and better understand the possible sources of the particulate matter deposited on samples. In this context, the comparison of soluble and carbon fractions detected during different atmospheric monitoring campaigns with those analysed on stone samples would provide useful qualitative and quantitative information about the component that can actually accumulate and potentially interact with stone substrate. Moreover, additional future analysis about changes of colorimetric parameters and soluble and carbon fractions deposited on stone surface will allow to better assess their reciprocal variation over time in order to set up damage functions.

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Presentations

Analysing pollutants deposition on carbonate stones exposed in different Italian urban sites

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Air pollution constantly threatens the conservation of stone used in historic built heritage of urban areas. Previous studies on pollution impact focused mainly on marble and limestone, due to their low porosity and chemical homogeneity, by analysing samples collected from historic buildings or performing tests in simulation chamber and/or in field. However, gaps still exist in measuring deposition fluxes on materials and developing proper solutions for long-term management of cultural heritage. Furthermore, the possible repercussions on built heritage of the current atmosphere, poorer than in the past of SO_2 but richer of NO_x and organic compounds, merit consideration.

Two years-long field exposure tests with model samples are currently under execution in Italian cities (Bologna, Ferrara, Florence) characterized by different environmental conditions as a non-invasive methodological approach for studying the impact of urban pollution on carbonate stones. The selected methodological approach as well as first available results on exposed samples after the first year of exposure will be discussed. Marble (Carrara Marble) and limestone (Red Verona Marble) were selected as model samples as they were widely used as construction and ornamental elements in historic Italian architecture. Galvanized metallic racks were prepared to host samples with different exposure orientations (i.e. horizontal, oblique and vertical) in order to identify how positioning may reflect on deposition and removal of pollutants. Stone samples were exposed outdoor, partially sheltered from the rain wash-out, in areas strongly affected by pollution due to vehicular traffic. At predefined time intervals, the exposed soiled specimens undergo mineralogical, petrographic and geochemical analyses (Optical Microscopy, Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis, Inductively Coupled Plasma Mass Spectrometry, Ion Chromatography analysis and Thermal-chemical methodology using a CHNSO combustion analyzer (Ghedini et al., 2006)) to characterise the damage products (typology, origin) due to the impact on stones by gaseous pollutants and carbon/soluble fractions of aerosol. Moreover, a connection between the deposited soluble and carbon fractions and changes of colorimetric parameters will be assessed for setting up damage functions, by performing colorimetric analysis. Simultaneously passive sampling of aerosol has been designed by the exposure of filters while seasonal environmental monitoring campaigns of particulate matter will allow to compare soluble ions and carbon fractions present into atmosphere with that actually accumulated on samples surface.

References
Ghedini N., Sabbioni C., Bonazza A. and Gobbi G., Chemical-Thermal quantitative methodology for carbon speciation in damage layers on building surfaces, Environmental Science and Technology, 40 (2006), 939-944.

SCIENTIA AD ARTEM3

Efficiency evaluation of nano-structured consolidants on Carrara marble by field exposure tests

Author: *Giorgia Vidorni*, graduated in Science for the Conservation-Restoration of Cultural Heritage (LM-11) at University of Bologna on 11 December 2014

Abstract

Since last century climate changes have become more influential in the weathering of built heritage and therefore the preservation of works of art is a priority for restorers and conservation scientists. In particular, available projections have evidenced that temperate Europe will undergo an increase in decohesion of carbonate stones. To reduce this problem, both organic and inorganic consolidants have been used but often their efficiency as well as the preliminary tests aimed at evaluating the real durability of new products proved to be questionable.

The thesis reports the results of the investigation in field on the efficiency, compatibility and durability of nano-based precursors for the deposition of calcium carbonate: the new calcium alkoxide (NANOMATCH1) synthesised within the activities of the 7FP EC NANOMATCH Project and CaLoSiL®, used as a reference. The performance of these products were analysed by field exposure tests on Carrara marble model samples exposed in cities characterised by different environmental conditions (i.e. Florence, Cologne, Oviedo, and Bucharest). In each site, samples were exposed outdoor, to the direct impact of rainfall for eleven months. Surface properties, superficial cohesion, distribution, penetration of the conservative products and their interactions with substrates and environmental agents were investigated by (i) colorimetric analysis, (ii) scotch tape test, (iii) optical microscopy and (iv) scanning electron microscopy coupled with energy dispersive x-rays spectroscopy. These results are compared also with those obtained from undamaged samples and those artificially damaged by thermal stress, since consolidants have to improve the physic-mechanical properties of damaged samples without altering the aesthetical features of the stone substrate. Analyses were performed before treatment, after treatment/before exposure and after eleven months of exposure.

The results obtained from the application of these products showed that they formed a homogeneous microcrystalline layer localized on substrate surface, with rare and superficial penetration, providing a superficial compactness of samples. The application of treatments displayed a general variation in total colour considered acceptable, higher in samples treated with CaLoSiL® than those treated with NANOMATCH1.

In general, the exposure of samples in the four sites entailed a reduction of material removed with peeling test, a rather acceptable change in total colour in all samples (lower in treated samples than in those artificially damaged) and a compactness loss of both marble and conservative materials. Moreover analyses under microscope indicated that the different environmental factors of each site implied dissimilarities between marble samples exposed in different cities and these variations were mainly induced by pattern and features of rainfalls.

Damage processes on stones in urban environment: field exposure tests and laboratory analyses contributing to pollution impact evaluation

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Stone conservation of historical built heritage in polluted atmosphere is an outstanding topic. In particular, the deposition, accumulation and interaction with the substrate of complex mixture of pollutant particles and gases can cause the formation of damage layers and, in consequence, entail chemical modification, physico-mechanical damages as well as aesthetic change of stone. Furthermore, environmental policies have recently restricted the concentration of atmospheric sulphur dioxide, considered as the most detrimental pollutant for carbonate materials, while an increase of nitrogen compounds, ozone and organic compounds due to higher vehicular traffic may lead to a chromatic variation of the damage layer and a probably growth in biological degradation. Until now, the impact of pollution on cultural heritage was studied by analysing samples collected from historic buildings or performing tests in simulation chamber and/or in field, but gaps still remain in developing damage and dose-response functions useful for the long-term management of cultural heritage sites and in measuring the deposition fluxes on materials.

The Institute of Atmospheric Sciences and Climate, ISAC-CNR (Bologna), in collaboration with the Department of Physics and Earth Sciences of the University of Ferrara, started in November 2015 a research work aimed at assessing the effect of urban atmospheric pollution on mainly carbonate sedimentary and metamorphic stones by performing field exposure tests in Italian cities characterised by different environmental conditions. The methodological approach selected for setting up the field tests and study the impact of pollution is presented.

As a first step the selection of the proper stone substrates, time and sites for the exposure and placement of the samples is carrying out. Specifically, the choice of the appropriate litotypes is factoring in marble and limestone widely employed in historic Italian architecture and characterised by an almost totally carbonate composition. Preference for samples exposure will be given to sites located outdoor, partially sheltered from the rain wash-out, in areas strongly affected by pollution due to vehicular traffic. The exposed samples will undergo mineralogical, petrographic and geochemical analyses (such as Optical Microscopy, Inductively Coupled Plasma Mass Spectrometry, Ion Chromatography analysis and Thermal-chemical methodology proposed by Ghedini et al. (2006) using a CHNSO combustion analyser), carried out in predefined time intervals, to characterise the deterioration products coming from the interaction between pollutants and stone substrate in terms of typology, origin and damage caused to stone. Moreover, the integration with colorimetric analysis will hopefully allow to identify a correlation between the deposited soluble and carbon fractions and changes of colorimetric parameters, for setting up damage functions. Finally, environmental monitoring of atmospheric particulate matter will be organised in order to acquire useful information from the comparison between the concentrations of pollutants deposited on stone substrate with those present in the atmosphere.

References

Ghedini N., Sabbioni C., Bonazza A., Gobbi G., Chemical-Thermal quantitative methodology for carbon speciation in damage layers on building surfaces, Environmental Science and Technology, 40 (2006), 939-944.

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