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Rainfall and Chemical Weathering of Basalt Facade at Puebla Cathedral, Mexico

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ABSTRACT

Pollutant emissions from anthropogenic activities have modified frequency, amount and chemical quality of rainfall at a specific site. Interactions of atmospheric dust with rainfall have induced weathering at Puebla Cathedral basalt facade. Chemical damage in exposed construction materials becomes evident as crusts, color bleaching, or salt deposits either into the stone or onto its surface. This work presents data on atmospheric dust (2012), rainfall (2009, 2011, 2012 years) and weathered basalt samples collected at downtown Puebla. Samples were characterized by gravimetric and spectrophotometric techniques for anions and metals. Results have provided evidence that atmospheric dust contains carbonates (>300 mg g^{-1}), sulfate and chloride (<10 mg g^{-1}); otherwise main anions in rain samples are bicarbonate>chloride>sulfate, this order is reproduced in the results of most weathered basalt samples.

1 Introduction

It is known that weathering of stone facades in ancient buildings is result of the climatic conditions at the place where they are located. For instance, it has been observed that limestone is prone to being deteriorated by the transformation of calcium carbonate into calcium sulfate, which is visible as white crusts; these become detached by contour scaling, multiple flaking or blistering. Other types of crusts can exhibit variations in color, morphology or thickness

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It is known that engines combustion release SO_2 and NO_X in the air. The SO_2 provides sulfide from anthropogenic sources, which can be absorbed through several routes such as absorption into the stone or in binding materials, as well as being transported by rising water as the phreatic level is modified in the site.

Reported studies have pointed that major weathering contributions come from rain and atmospheric dust, as example can be cited a Budapest study (Siegesmund et al, 2007) in which authors mapped two walls at the Citadella with different exposure conditions to wind and rainfall, they found that weathered samples, in respect to the unweathered reference, exhibit white crusts which have sulfur ranging between 0.5-5.6 wt %, and they exhibit a gradual increase from the ground level upward. Also they found that granular disintegration took place in low lying rows. Black crusts were found in those places sheltered from rainfall, and the percentage of covered areas slightly decreases from the ground level upwards.

A report about black crusts on travertine (Török, 2008), refers that there are laminar and framboidal crusts with variations in thickness and gypsum content; compound which is absent in fresh travertine; crusts mineralogical analysis shown that gypsum occurs in all crusts and even in atmospheric dust, the last one is rich in quartz and contains 28% gypsum and 5% calcite. Another report on black crusts (Ortiz et al, 2010) agrees in statement that the main weathering product is gypsum, which is related to sulphur oxides in the atmospheric environment; also, surface alteration and the depth of the damage is clearly defined by the stone porosity, as well as deposits of dust and anthropogenic particles, which are producing surface alteration.

Another approach in heritage preservation is to estimate the impact of gaseous air pollutants (Kontozova-Deutsch, 2008) findings indicate that indoor most abundant particles can be classified as: soil dust, organic, carbonate, ammonium nitrate. Also, it is considered that chemical composition of indoor particles is more dangerous than the one of particles sampled outdoors.

About atmospheric dust characterization, some reports (Kyotani and Iwatsuki, 1998; Bourotte et al, 2005) agree that dust particles should be characterized considering the water and acid soluble components, applied extraction techniques range from the simple approach of preparing an analytical sample with distilled water up to sophisticated methods like Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Reported results for metals have provided evidence that the higher soluble concentration is obtained within the first extract; also, in order of abundance sequence of extracted main anions should be $SO_4 > Cl > NO_3$; while main metals abundance corresponds to the sequence Ca>Na>Mg. Finally, anthropogenic activities make that urban dust chemical composition raises in sulfate concentration, while dust from the rural areas become high in chloride from marine source; also Boogaard et al (2011) has provided evidence on how particle composition, black carbon and NO_2 presence can be considered as indicators of non-exhaust emissions

In this report it is presented main findings in atmospheric factors taking place at downtown Puebla such as rainfall and atmospheric dust, chemical properties of both are correlated with chemical composition found in weathered basalt at the Cathedral of Puebla.

2 Methodology

Samples of rainwater, weathered basalt and atmospheric dust were collected, the last two were mixed with water to get the soluble ions, and acid digested to get the total metal concentrations.

2.1 Rainfall chemical analysis

Rainfall was collected during three seasons (2009, 2011, 2012); samples of 2009 were exhaustively characterized for pH, conductivity, anions (chloride, hardness, alkalinity, sulfate, nitrate and phosphate) and metals (sodium, iron, cobalt, lead, nickel, copper, manganese, cadmium, zinc, magnesium and calcium), results were used to build an statistical analysis matrix, finding that rainwater composition has an input from atmospheric dust (Teutli et al, 2010). From chemical results of the 2009 season, it was possible to establish the main ions to be determined, and so far to shorten the number of parameters.

2.2 Weathered basalt chemical analysis

From historical records it is known that Cathedral facade basalt was extracted from the Bethleem quarry at Puebla; from this place it was possible to get an unweathered sample which is included as reference. Visual inspection of the Cathedral facade was used to detect weathered sites, and scrap samples that were mixed with water (1:2 ratio) and chemically characterized for the following parameters: pH and conductivity; carbonate determined by the Bernard calcimeter method; gravimetric techniques were used for hardness, alkalinity, and chloride; otherwise, spectrophotometric techniques were applied for sulfate, nitrate and phosphate.

2.3 Atmospheric dust chemical analysis

Atmospheric dust was collected inside of the Cathedral of Puebla, and outside at the roofs of three buildings at downtown Puebla (Civil Engineering Board, Colonial Hotel and Saint Agustin Temple); these samples were mixed with distilled water (1:2 ratio) and analyzed for pH, conductivity, carbonates, chloride, hardness, alkalinity, sulfate, nitrate, and sulfide. Also metal concentration soluble and total (from acid digestion) were analyzed by atomic absorption spectroscopy; determined metals comprise aluminum, copper, manganese, lead, zinc, calcium and iron.

3 Results and discussion

Considering that reported data comprise liquid samples (rainwater), and two kind of solid samples (atmospheric dust and weathered basalt), is considered to present chemical composition of each kind of samples, and after that set up the correlation between them. Data presented in this paper are the synthesis of three sets of experimental data.

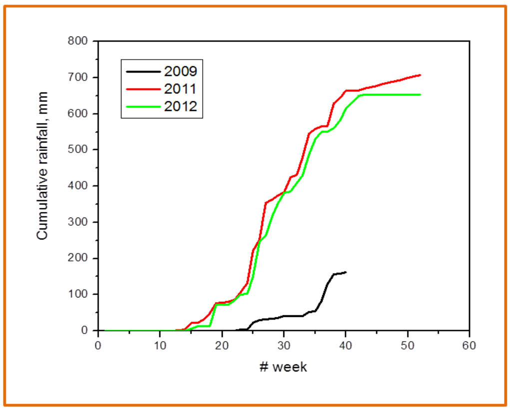

Figure 1: Cumulative rainfall registered at downtown Puebla.

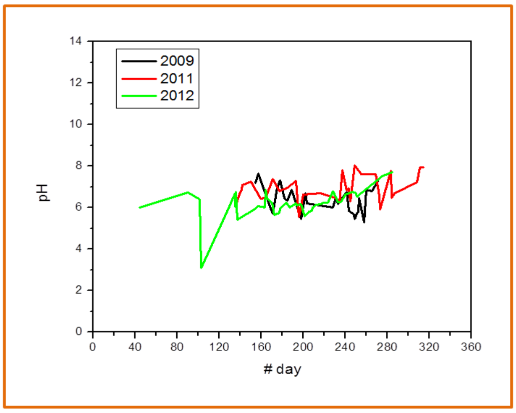

Figure 2. Rainfal pH values at downtown Puebla.

3.1 Rainfall chemical characterization

Figure 1 present the cumulative rainfall of the three years 2009, 2011, 2012 data were obtained from a government meteorological page (Comisión Nacional del Agua) and corresponds to an average of the precipitation that took place at downtown Puebla, but not necessarily rain felt at the place where the collection was done. As it can be observed, in 2011 and 2012, similar quantities of rain were obtained, otherwise 2009 was an almost dry year since the season started very late and cumulative volume was less than 25% with respect to the other seasons; also, this year exhibit a long period of dryness and rainfall stops about to the 260th day, while 2011 stopped at the 300th day, and 2012 about the 320th day.

Figure 2 presented data for pH. It can be observed strong variations of pH took place at the beginning of the 2012 season, in which the 100th day sample exhibit an acid pH (<3), but after the 140th day pH started to oscillate between 5.5 and 8.0, so far rainwater has not strong acidic characteristics.

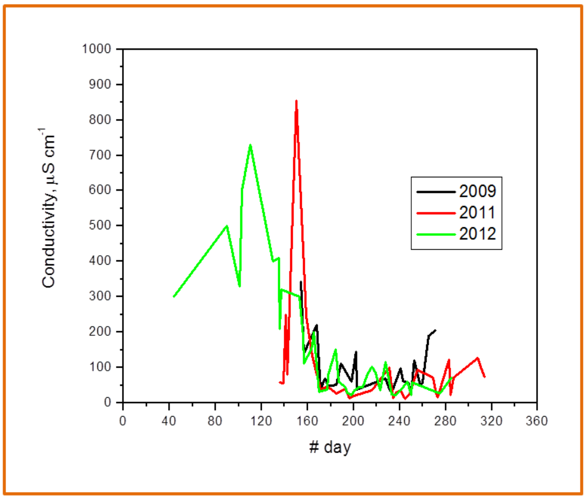

Figure 3: Rainfal conductivity values for downtown Puebla.

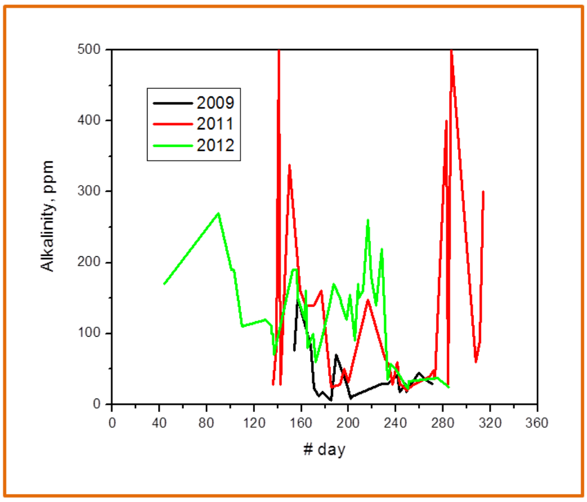

Figure 4: Rainfall alkalinity values at downtown Puebla

In Figure 3 are presented results of the electrical conductivity in this plot it is clear that higher conductivity values took place at the beginning of the rain season, and it happens that both 2011 and 2012 exhibit a rising trend before the 160th day, except for the 100th day of the 2012 (with lower pH), where it happens that conductivity exhibits a drop to a value closer to the one registered at the beginning of the season. It is after the 160th day that conductivity drops to values below 150 mS cm^{-1}. At this time is considered that rainfall has been enough to wash out the pollutants in the downtown atmosphere, the amount is about 100 mm of rain.

In Figure 4 are presented results for total alkalinity, this parameter includes HCO_3, CO_3, OH, this set of data mainly represents an estimation of the ability to neutralize acidic pollution. As it can be observed 2011 was the year with higher values, around the 140th day concentration was close to 500 ppm, and a similar value is observed at the 280th day. A lower amount was observed for rain in 2012 since values never get higher than 280 ppm; also most values oscillate between 50-150 ppm; otherwise, 2009 was the year with the lower alkalinity since a maximum registered on the 160th day was less than 150 ppm. In general for the three years most of the values were smaller than 200 ppm.

The second anion in order of importance was chloride (Cl^-), results are shown in Figure 5, as it can be observed most of the values are between 20 and 80 ppm. A separate analysis indicates that top values for 2011 were about 200 ppm at the 140th and 300th days; otherwise, 2012 only reached two top concentrations around the 100th and the 130th days, and a minimal almost at the end of the season. Finally 2009 was a year with the lowest concentration and a top value happened almost at the end of the season, this was a consequence of heavy precipitation, fact which is in agreement with the statement that Cl presence mainly comes from marine source.

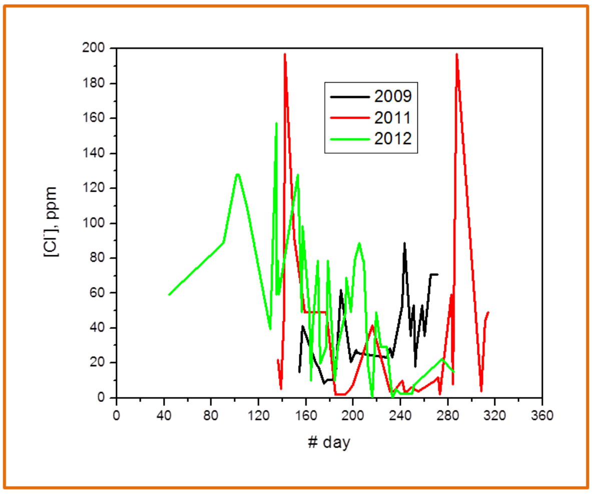

Figure 5: Rainfall chloride values at downtown Puebla

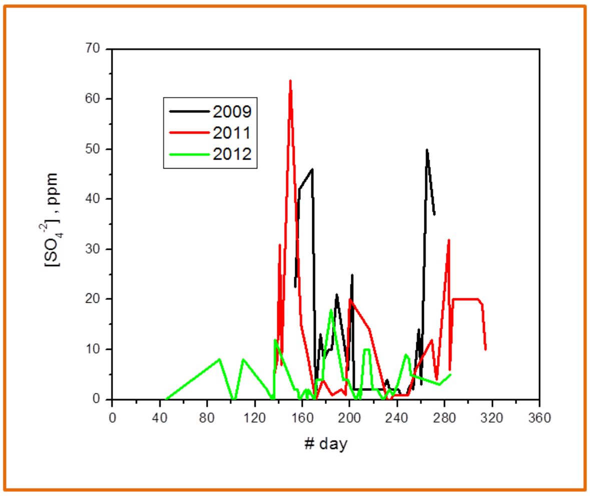

Figure 6: Rainfall sulfate data for downtown Puebla

Figure 6 shown the data for sulfate (SO_4^{-2}) and as it can be observed most values are between 5- 20 ppm, but between the 140th and the 170th days higher sulfate concentrations were registered for 2009 and 2011, and even though that 2009 was the year with low precipitation. Sulfate values are really high in the first precipitations. Also there is another period with high concentrations between 260th and 280th days, the one for 2009 even get a higher value than the observed at the beginning if the season. Otherwise, 2012 was a season that started very early (40th day), therefore the early atmosphere wash out did not allow concentration to exceed the 20ppm.

Figure 7 presented the nitrate (NO_3) results. As it can be observed most of the values lie between 0.5-3 ppm, this anion does not follow a consistent pattern since in 2009 higher values occured at the beginning and end of the season, as it happened with sulfate; otherwise, for 2011 highest concentrations took place between the 140th and the 160th days and exhibit another raise almost at the end of the season but in magnitude less than 50% of the one registered at the beginning. An anomalous behavior occurs with the 2012, since higher values were registered after the 160th day, and values at the end of the season are even higher than the ones from the other years.

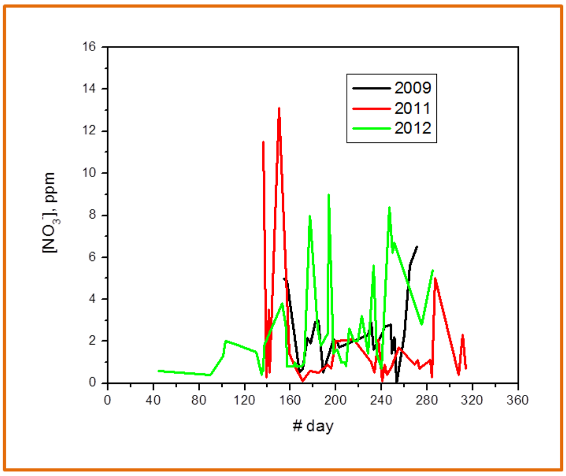

Figure 7: Rainfall nitrate data at downtown Puebla.

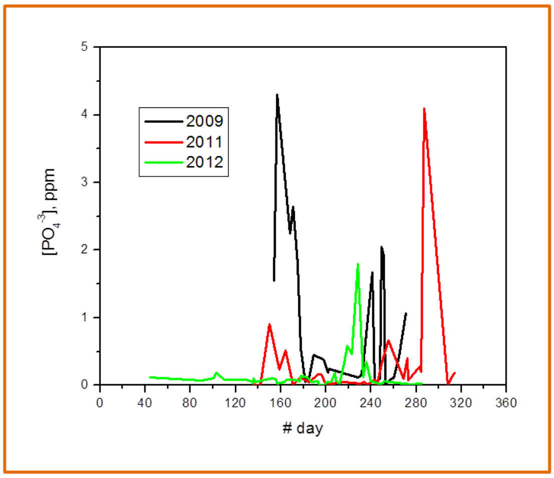

Figure 8: Rainfall phosphate data at downtown Puebla

In general, phosphate (PO_{4-}^{3}) concentrations are lower than the ones observed for nitrate, results are presented in Figure 8. As it can be observed most of the values are below 1 ppm; also, trends are completely different for all years, since 2009 exhibit a maximum at the beginning of the season; and another peak, of lower intensity before the end of the season; in opposite way 2011 exhibit only one maximum and this occurs almost at the end of the season, while 2012 exhibit a maximum at the middle of the season which is not greater than 2 ppm., although, there is presence of some peaks in concentration.

3.2 Weathered basalt chemical characterization

Basalt samples were collected at the main façade (west side, low rainfall impact), at the lateral facade (north side, high rainfall impact), also in the north tower (faces oriented north, east, south and west). Chemical characterization results are reported in Table 1. Collected samples were 19, and it is included a sample of unweathered basalt as reference.

From data in Table 1, it can be observed that pH values in general are more acid than the reference; also, the higher observed pH is about 80% of the reference. Electric Conductivity (E. C.) results can be grouped as follow: 3 samples with lower concentration in respect to the reference, and a higher one which is about 7 times the reference (558 ppm). Total carbonate in all samples is higher than the reference content, the lower value observed is about 4 times the reference and the higher value is about 25 times the reference. From these results it can be assumed that higher ionic content can derive in fragility of the stone.

Table 1: Data of weathered basalt.

Sample #	Location	Orientation	Height, m	pH	E.C. µS cm^{-1}	$CaCO_3$ g Kg^{-1}
0	Reference			8.62	80	11.00
1	Main Facade	West	18.00	5.78	70	296.67
2	North Tower	North	30.00	4.48	186	204.69
3	North Tower	North	42.00	3.83	242	160.58
4	Main Facade	West	1.50	3.62	558	40.00
5	Main Facade	West	1.50	6.81	82	233.55
6	Main Facade	West	1.35	4.01	93	212.06
7	North Tower	North	30.00	5.89	120	170.00
8	North Tower	North	42.00	6.02	106	251.71
9	North Tower	South	42.00	6.19	177	136.34
10	North Tower	South	42.00	6.44	180	173.35
11	North Tower	East	42.00	6.48	175	151.18
12	North Tower	South	30.00	6.39	71	180.95
13	North Tower	East	30.00	3.82	162	135.41
14	Main Facade	West	0.10	6.81	57	64.90
15	Main Facade	North	0.50	6.93	382	196.87
16	North Tower	East	30.00	6.44	227	173.00
17	North Tower	West	30.00	6.89	153	194.97
18	North Tower	East	42.00	6.89	92	134.39
19	North Tower	West	42.00	5.91	389	169.00

Table 2 presented data of soluble anions found in the basalt samples, these data were restricted to the main anions found in the rainfall chemical data.

From these data it is obvious that anions contribution in weathering basalt can be arranged in order of importance such as: carbonate>sulfate>chloride>alkalinity>nitrate>phosphate; in this sequence only nitrate and phosphate match with the rainfall data. Also, it is worthy to point out how each parameter behaves in respect to the reference.

For total alkalinity all values are above the reference, the lower value is almost 25 times, while the higher one is almost 63 times; chloride is absent in the reference and the higher value in samples is 14.2 g Kg^{-1}; sulfate is present in the reference but weathered basalt exhibits values lower (2/19), and only two exhibit really high concentrations, the maximum one is almost 100 times the reference; nitrate exhibit a singular response since 8/19 samples have lower values, and 10/19 have higher values with a maximum which is about 8 times the reference; about phosphate 2/19 samples are lower than the reference and the maximum reached up to 10 times the reference. In general it can be said that order has been traslocated in respect to the rainfall since in order of abundance, the sequence is sulfate>chloride>alkalinity.

Table 2: Main water soluble anions in weathered basalt.

Sample #	Location	Alkalinity g Kg^{-1}	Chloride g Kg^{-1}	Sulfate g Kg^{-1}	Nitrate g Kg^{-1}	Phosphate g Kg^{-1}
0	Reference	0.02	0	1.50	0.08	0.02
1	Main Facade	0.84	10.60	7.58	0.11	0.03
2	North Tower	1.10	3.67	127.93	0.49	0.02
3	North Tower	0.53	9.98	2.72	0.02	0.01
4	Main Facade	0.79	3.71	169.40	0.15	0.17
5	Main Facade	0.55	14.02	2.87	0.05	0.08
6	Main Facade	0.51	9.72	6.86	0.00	0.09
7	North Tower	0.56	7.07	4.98	0.32	0.03
8	North Tower	0.53	3.70	2.76	0.28	0.12
9	North Tower	0.78	0.00	7.04	0.37	0.04
10	North Tower	0.55	3.46	7.42	0.64	0.12
11	North Tower	0.54	10.30	6.97	0.38	0.02
12	North Tower	0.56	3.52	7.54	0.33	0.09
13	North Tower	0.54	6.84	5.98	0.09	0.06
14	Main Facade	0.81	3.41	0.67	0.06	0.11
15	Main Facade	0.80	6.79	0.19	0.06	0.01
16	North Tower	0.80	0.00	2.10	0.18	0.13
17	North Tower	1.26	10.59	2.84	0.16	0.09
18	North Tower	0.56	3.51	2.87	0.04	0.04
19	North Tower	0.54	3.43	7.36	0.05	0.19

It is important to focus on location of collection points taking as reference orientation and height, then a comparison is done for samples #2 (north, 30 m), #4 (west, 1.5 m) and #10 (south, 42 m) for the parameters carbonate, pH, alkalinity and sulfate. These samples are compared in function of its position and exposure to rain and wind. Samples #2 and #10 were collected at an horizontal place but different height and orientation, then there is high probability that dust become accumulated and by rainfall action being dissolved and penetrate into the basalt matrix; otherwise, sample #4 was collected in a vertical place almost at the ground level, so far it is possible that dust and rainfall approach the wall, and slip downwards; in this path dust will be solubilized and carried on to the floor level. Data are presented in table 3

Table 3: Weathered basalt comparison as function of its orientation

Sample #	$CaCO_3$ g Kg^{-1}	pH	Alkalinity g Kg^{-1}	Sulfate g Kg^{-1}
2	204	4.48	1.10	127.00
4	40	3.62	0.79	169.00
10	173	6.44	0.55	7.42

As it can be observed sample#4 (vertical position) has a low carbonate content in respect of samples #2 and #10, and so far is expected a lower pH, favoring sulfate accumulation which could come from solubilization of gaseous sulfur dioxide (SO_2) . Focused on sulfate content pH of sample #2 should be more acid, but both alkalinity and carbonate are higher than the ones in sample #4, and so far a neutralization could take place increasing the pH. Otherwise, sample #10 was collected at the south side of the north tower, so far this side has lower exposition to rain and wind than the north side and that fact could explain why pH is higher correlating well with the low sulfate content.

3.3 Atmospheric dust

Samples to determine chemical composition were collected at two environments: samples #1-5 come from the interior of the Cathedral; while samples #7-9 were collected at the roofs of three buildings with different vehicular density. Data are reported in Table 4.

Table 4: Atmospheric dust data.

Sample #	Location	pH	$CaCO_3$ g Kg^{-1}	Chloride g Kg^{-1}	Sulfate g Kg^{-1}	Nitrate g Kg^{-1}	Phosphate g Kg^{-1}
1	Sacristy	5.56	278	1.44	11.25	0.97	0.00
2	Candle soot	6.14	346	10.07	46.72	3.85	0.01
3	Main entrance	6.83	343	0.33	5.93	0.003	0.1
4	Choir, Southeast	7.23	278	0.31	5.47	0.27	0.00
5	Choir South	6.6	299	1.65	29.38	1.04	0.00
6	Choir west	6.2	302	0.00	16.82	0.37	0.00
7	Eng Board Roof	7.84	364	5.48	5.9	0.30	0.00
8	Colonial Hotel roof	6.36	359	8.91	0.50	0.54	0.00
9	Saint Agustin roof	6.62	304	4.45	3.40	0.19	0.00

From these data it can be observed that pH exhibit moderate values which fall between 5.5 and 8. But most of the values are close to the average in weathered basalt which is 5.78. Carbonate content is between 270 and 370 g Kg^{-1}, values which are above the ones detected in weathered basalt, since the higher value was 296 and the average was 170 g Kg^{-1}. In respect of chloride it becomes evident that dust at inner spaces has very low content except the sample of the candle soot, otherwise samples collected outdoors are closer to the average value of weathered basalt (6.2 ppm). Sulfate data show a higher value in the candle soot, and the sample collected at the Choir, and all others are below the average value in weathered basalt. Nitrate values are higher in respect to the average found in weathered basalt (0.2 ppm) and again the candle sooth exhibit the higher concentration. Phosphate presence is almost null and only the candle soot and the sample from the main entrance are higher than the average value of weathered basalt (0.08 ppm).

4 Conclusion

From rainfall data, it was observed that anions in order of abundance follow the sequence: alkalinity>chloride>sulfate>nitrate>phosphate, while the corresponding sequence for weathered basalt is being traslocated as sulfate>chloride>alkalinity>nitrate>phosphate, and in atmospheric dust it is observed the sequence sulfate>alkalinity>chloride>nitrate>phosphate. Also this sequence agrees with findings reported by Kiotani and Iwatsuki (1998), and Bourotte at al (2005).

It can be affirmed that main contribution in rainfall is alkalinity, which is high enough to avoid acidic pH occurrence in most of the collected samples.

For diagnosis of weathering in heritage buildings is important to account for location, orientation and height. In this study, results have shown that incorporation of sulfate is highly dependent of how the stone structure is located (horizontal, vertical), its orientation in respect of main incidence of rain and wind, as well as it height since lower sites are more prone to accumulate soluble compounds.

5 References

Boogaard, H., Kos, G. P. A, Weijers, E. P., Janssen, N. A. H., Fischer, P. H, Van der Zee, S., Hartog, J. J., Hoek, G. (2011). Contrast in air pollution components between major streets and background locations: Particulate matter mass, black carbon, elemental composition, nitrogen oxide and ultrafine particle number. Atmospheric Environment, vol 45(3), pp. 650-658.

Bourotte, C., Forti, M. C, Melfi, A. J., Lucas, Y. (2005). Morphology and solutes content of atmospheric particles in an urban and a natural area of Sao Paulo State, Brasil. Water, Air, and Soil Pollution, vol 170(1-4) pp. 301-316.

Comisión Nacional del Agua (CNA). Metereological stations. www.*smn.cna.gob.mx › Climatología*

Kyotani, T., Iwatsuki, M. (1998). Determination of water and acid soluble components in atmospheric dust by inductively coupled plasma atomic emission spectrometry, ion chromatography and ion-selective electrode method. Analytical Sciences, vol 14(4), pp. 741-748.

Kontozova-Deutsch, V.,Moreton Godoi, R. H., Worobiec, A., Spolnik, Z., Krata, A., Deutsch, F., Van Grieken, R. (2008). Investigation of gaseous and particulate air pollutants at the Basilica Saint Urban in Troyes, related to the preservation of the medieval stained glass windows. Microchimica Acta, vol 162(3-4), pp. 425-432.

Ortiz, P.,Vázquez, M. A., Ortiz, R., Martin, J. M., Ctvrtnickova, T., Mateo, M. P., Nicolas, G. (2010). Investigation of environmental pollution effects on stone monuments in the case of Santa maria La Blanca, Seville (Spain). Applied Physics A. Materials Science & Processing, vol 100(3), pp. 965-973.

Siegesmund, S., Török, A., Hüpers, A., Müller, Chr., Klemm, W. (2007). Mineralogical, geochemical and microfabric evidences of gypsum crusts: a case of study from Budapest, Environmental Geology, vol 52(2), pp. 385-397.

Teutli León, M., Jiménez Suárez, G., Peláez Cid A. A., Lozano Mercado, J., Posada Sánchez A. E. (2010). Rainfall chemical composition at Puebla, México. Enlace Químico, vol 2 (9), December 2010.

Török, A. (2008). Black crusts on travertine: factors controlling development and stability. Environmental Geology, vol 56(3-4), pp. 583-594.

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