Investigation on Urban Rain Pollution, a Case of Study: Rain Over Rome

Maria Pia Sammartino, Giovanni Visco, Mauro Tomassetti, Luca Ugo Fontanella

Chemistry Department, "La Sapienza" University, p.le A. Moro 5, 00185, Rome, Italy

Introduction

The composition of rainwater is the result of complex interactions between the water vapour of the clouds, the dust raised by the wind and the atmospheric gases. The chemical composition of rainfall can probably be related to local sources of pollution in urban areas, but also to relatively distant sources, provided that there is an atmospheric transport phenomenon.

The pH of rainfall depends essentially on the result of neutralizing reactions between the acid components of rainwater [1], mainly derived from acid gases such as carbon dioxide, nitrogen oxides and sulphur oxides, and the basic components, mainly ammonia, bicarbonates, carbonate and hydroxides of calcium and magnesium. The latter coming mainly from erosion phenomena. The presence of other metals in the rains seems to be linked, in addition to erosion phenomena, also to their presence in fossil fuels which, during combustion, produce oxides which are then hydrated by the water in the cloud. This presentation shows the results of the monitoring of chemical-physical data of rain samples fallen in Rome during 7 months on the year 2018.

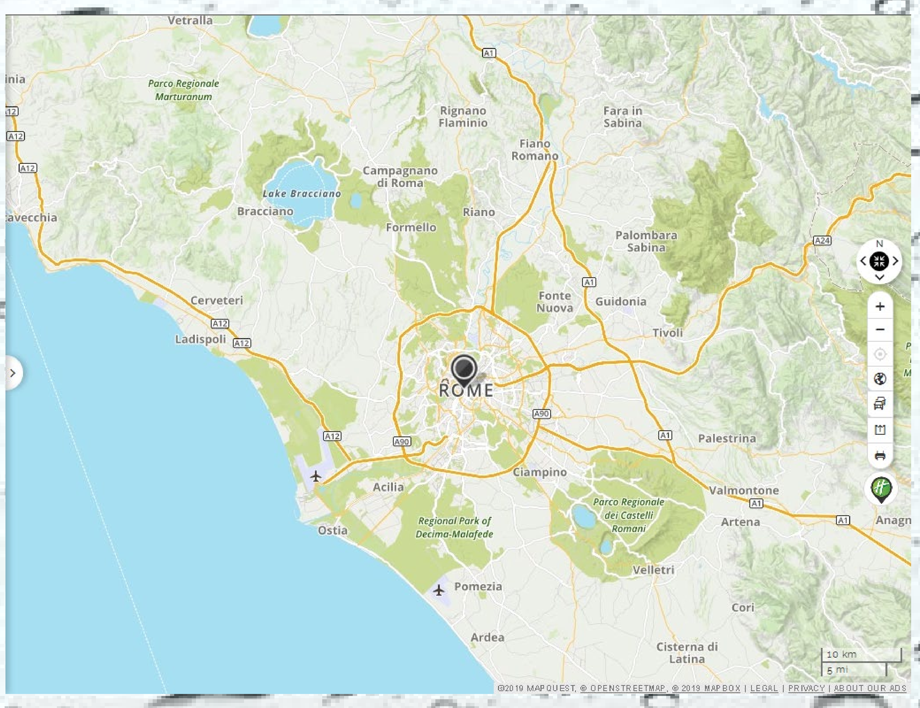

Fig.1, the map urban area of Rome and surrounding, see the Tyrrhenian Sea on west

Aim of Research

Data on rain composition should have a great interest given the large number of monuments and archaeological finds exposed outdoors in the city of Rome. Despite the importance of the subject there are no major studies published recently on the rain that fell on Rome since 1971 [2]. The present experimental study seeks to fill this gap, at least in part.

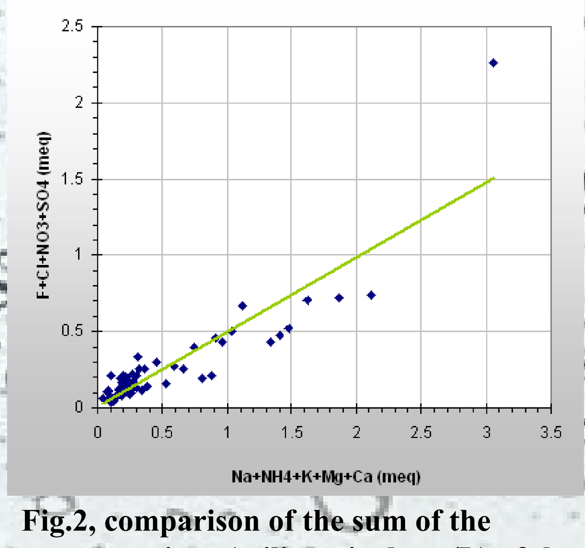

Fig.2, comparison of the sum of the concentrations (mili-equivalents/L) of the main cations vs. anions

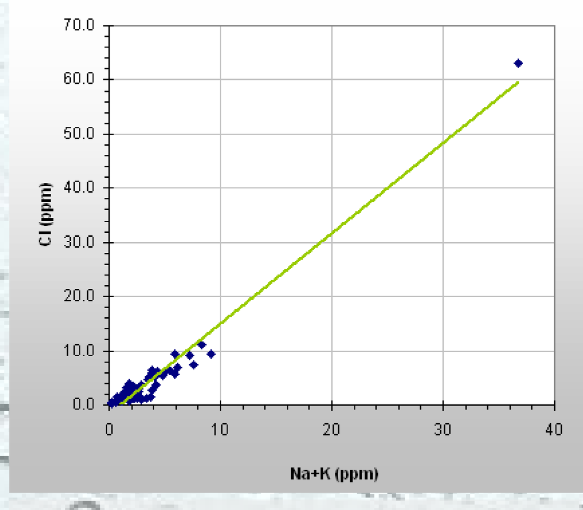

Fig.3, correlation between the sum of Na^+ and K^+ concentrations vs. Cl^- ion

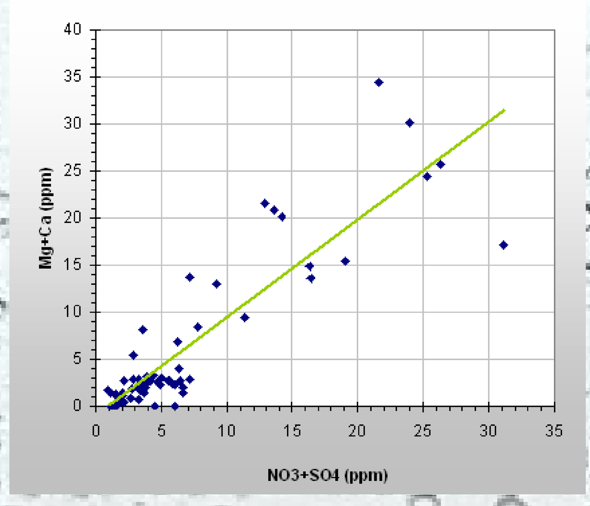

Fig.4, correlation between the sum of NO_3 and SO_4 concentrations vs the sum of Mg^{++} and Ca^{++} ions

Sampling and analysis

We collected 62 rain samples between January and July of 2018, the rain was collected every day on the roof of the Department of Chemistry of the University "La Sapienza", Rome (Fig. 1). The sampled rain was poured into Falcon tubes kept at 4 °C, a part of the rain was used for immediate direct analyses, the other used for ion chromatography. The direct analyses were performed with bench top instruments and electrodes (by Vernier, USA) and covered the pH, conductivity, temperature and redox potential (ORP).

At the same time the data on speed and wind direction were acquired, in order to find a correlation between the variations in the composition of the rains and the ion transport phenomena [3], data obtained from the weather station of Piazza Galeria, about 4 Km from the sampling point and data on the volume of rain fell and its temperature were collected from the weather station in the Civil Engineering headquarters, in Via Mozambano, about 500 meters from the sampling point.

Results

All data collected and experimentally obtained in this research are shown in table 1 that reports: the sampling data, the volume of rain fallen in that day as mm of rain (1 mm of rain= 1L/m²), atmospheric pressure of rain's day, the temperature of the rain and the number of days elapsed since the last precipitation preceding the day of sampling. In the same table the values obtained from the measurements of pH, conductivity and ORP were reported, finally values of the cation's concentrations (sodium, potassium, ammonium, magnesium and calcium) and anions (fluoride, chloride, nitrate and sulphate) have been reported. In Tab.1 some day are put in evidence with colours and can be presented in the next paragraph.

The general observations can be made by reading table 1 are: first of all, the rain fell in Rome in a very discontinuous way, while the fallen volume of rains was generally between 20 and 0.5 L / m. The rain pH was always higher than 5 consequently no authentic acid rains were recorded [4], finally, the redox potential of the samples was rather stable, around 350 mV, while the conductivity varied considerably. In IC analysis each rain sample was analyzed three times, the quantification limit for anions is 0.2 mg / L, while for cations it is 1 mg / L, the accuracy of the measurement, calculated as the standard deviation among the samples analyzed is about 5% for cations and 2% for anions.

Tab.1: Chemical physical characterization of Rome's urban rainwater, from 01 February 2018

date	Acidity pH	Redox pot. mV	Conductivity uS	Rainfall mm	Temperature °C	Pressure mm Hg	n. days before	Na ppm	NH4 ppm	K ppm	Mg ppm	Ca ppm	F ppm	Cl ppm	NO3 ppm	SO4 ppm
2-Feb-18	6.57	346	157.0	2.6	14.2	750.1	2	2.8	1.9	4.8	0.6	20.2	0.00	7.5	3.7	9.8
3-Feb-18	6.26	345	21.9	12.2	11.4	744.7	1	1.1	0.7	0.7	0.1	2.1	0.14	1.3	2.7	2.2
4-Feb-18	5.84	363	28.2	2.2	6.3	755.9	1	1.6	0.5	0.8	0.2	2.3	0.19	1.2	3.3	2.5
5-Feb-18	6.56	327	48.4	1.0	10.0	760.5	1	2.4	1.5	1.8	0.2	8.3	0.13	3.7	3.7	4.1
7-Feb-18	6.35	329	26.6	12.8	10.3	747.8	2	0.7	0.5	0.5	0.1	2.5	0.18	0.8	2.6	2.1
12-Feb-18	6.20	384	78.9	0.6	6.3	754.2	5	3.8	1.2	1.6	0.6	14.3	0.13	6.4	5.9	10.4
18-Feb-18	6.30	361	24.4	6.0	10.8	748.7	6	1.2	0.5	0.2	0.1	1.4	0.00	2.0	1.9	1.7
19-Feb-18	6.40	321	23.4	0.8	8.4	750.3	1	1.5	1.4	1.1	0.6	14.9	0.07	2.5	8.7	10.5
22-Feb-18	6.34	361	22.2	12.0	7.4	752.5	3	0.9	0.8	0.5	0.1	2.1	0.05	1.4	1.9	1.8
23-Feb-18	5.50	360	13.5	25.6	9.6	756.9	1	0.2	0.0	0.0	0.0	1.8	0.00	0.5	0.4	0.6
24-Feb-18	5.50	357	18.8	7.4	10.8	746.1	1	0.7	0.9	1.1	0.3	0.8	0.25	1.5	1.1	0.8
25-Feb-18	6.54	332	15.5	7.2	7.8	750.8	1	0.7	0.5	0.7	0.1	1.2	0.08	1.2	0.9	0.7
26-Feb-18	5.20	376	17.7	7.4	0.3	754.6	1	0.8	0.6	0.9	0.2	0.9	0.16	1.6	1.2	0.9
28-Feb-18	6.65	331	94.5	1.0	0.1	752.5	2	3.0	0.9	1.2	0.6	13.0	0.00	5.2	6.8	9.7
1-Mar-18	5.58	353	35.0	2.0	5.2	752.0	1	1.4	1.1	0.8	0.0	2.6	0.00	1.9	2.2	1.8
2-Mar-18	5.90	380	121.0	0.8	8.4	750.5	1	6.9	0.4	1.4	1.4	33.0	0.00	11.1	5.5	16.1
3-Mar-18	6.18	361	31.1	9.4	10.8	749.1	1	3.2	0.3	0.6	0.0	0.0	0.00	5.8	0.5	1.0
4-Mar-18	5.83	351	19.0	7.6	10.7	747.7	1	1.5	0.5	0.7	0.0	5.4	0.29	2.6	1.3	1.5
5-Mar-18	6.17	340	15.2	18.4	11.0	743.6	1	0.5	0.3	0.5	0.0	1.4	0.00	0.8	0.7	0.5
6-Mar-18	6.29	357	18.2	18.8	11.6	747.5	1	1.3	0.3	0.3	0.0	0.0	0.00	3.1	0.7	0.6
7-Mar-18	6.26	347	23.3	4.4	11.6	749.0	1	1.6	0.5	0.2	0.0	0.0	0.00	4.0	5.3	0.7
11-Mar-18	6.33	323	37.7	5.8	15.5	751.6	4	1.9	0.2	0.1	0.2	2.7	0.00	3.2	1.3	1.5
12-Mar-18	6.22	353	29.9	10.4	14.3	750.1	1	2.4	0.4	0.5	0.4	2.6	0.08	1.2	2.7	2.2
15-Mar-18	6.30	326	55.8	0.6	12.2	754.6	3	3.3	1.3	1.5	0.0	4.0	0.27	5.8	2.8	3.5
16-Mar-18	6.71	333	73.4	1.4	15.4	750.8	1	3.5	1.2	1.6	0.3	9.1	0.20	6.1	4.4	7.0
17-Mar-18	6.87	339	98.5	1.8	12.8	743.2	1	5.6	0.8	1.6	1.3	28.8	0.00	9.0	7.3	16.7
18-Mar-18	6.33	333	36.5	15.8	11.2	741.7	1	2.9	0.6	0.8	0.0	0.8	0.00	5.3	0.8	1.8
19-Mar-18	6.31	338	27.7	12.4	10.1	744.7	1	1.3	0.5	0.9	0.1	2.2	0.23	1.2	3.5	2.5
20-Mar-18	6.48	340	19.4	8.6	10.6	749.3	1	1.5	0.3	0.2	0.0	0.0	0.00	2.8	0.9	0.6
21-Mar-18	6.15	346	19.2	7.8	8.2	750.8	1	1.5	0.4	0.5	0.0	2.7	0.14	2.7	1.1	1.1
26-Mar-18	7.06	294	34.8	0.8	8.7	750.8	5	1.5	1.1	0.9	0.0	2.7	0.00	2.4	3.0	2.6
30-Mar-18	7.25	276	33.0	0.8	15.4	754.6	4	1.2	0.9	0.1	0.2	13.6	0.14	2.2	4.9	2.2
31-Mar-18	6.39	322	25.5	14.2	13.7	748.5	1	1.6	0.5	0.2	0.2	2.9	0.07	0.8	2.0	1.9
4-Apr-18	6.90	261	125.0	0.8	13.9	759.7	4	35.1	2.4	1.7	4.4	20.1	0.23	63.0	11.3	14.0
5-Apr-18	6.80	265	20.0	7.4	14.1	756.7	1	1.5	0.5	0.9	0.0	8.2	0.43	2.4	1.6	2.0
9-Apr-18	7.15	290	15.0	37.2	14.8	750.8	4	0.7	0.1	0.1	0.0	0.0	0.00	1.6	0.6	0.6
11-Apr-18	6.72	315	31.9	0.6	15.7	751.8	2	3.5	0.8	0.8	0.2	2.5	0.13	6.2	1.8	2.3
12-Apr-18	7.14	304	18.0	0.6	16.4	750.8	1	3.8	0.2	0.1	0.4	1.1	0.00	6.5	0.9	1.2
3-May-18	6.46	337	163.0	4.2	19.5	744.7	21	3.3	1.7	5.8	0.5	21.0	0.00	9.4	2.4	10.5
4-May-18	6.09	372	21.5	3.4	18.1	749.3	1	1.0	0.9	0.9	0.0	2.3	0.01	1.6	2.0	1.6
7-May-18	6.68	355	151.0	1.8	18.9	756.7	3	2.2	2.1	3.7	0.7	19.4	0.00	5.6	5.1	9.1
8-May-18	6.23	385	4.0	53.4	18.1	753.1	1	0.2	0.3	0.5	0.0	0.4	0.00	0.6	1.0	0.8
9-May-18	6.17	407	9.0	25.2	18.2	750.8	1	0.4	0.7	0.8	0.0	0.5	0.00	1.0	1.1	1.0
10-May-18	6.28	399	11.0	7.0	19.0	753.1	1	0.4	0.8	0.3	0.0	0.0	0.00	0.8	2.5	1.9
13-May-18	6.33	405	33.0	5.0	19.6	756.7	3	1.7	1.0	0.9	0.0	2.8	0.00	2.9	3.8	3.4
14-May-18	6.55	393	38.0	0.4	17.9	754.6	1	5.5	0.3	0.4	0.2	0.5	0.00	9.5	0.9	2.4
15-May-18	6.40	397	15.0	15.8	14.9	756.7	1	1.7	0.4	0.4	0.0	1.2	0.00	2.9	0.7	0.9
16-May-18	6.36	342	93.2	4.4	15.1	757.4	1	1.6	0.7	0.6	0.0	1.4	0.00	3.5	4.6	2.0
21-May-18	6.50	388	136.0	0.6	20.1	755.4	5	1.8	1.8	2.1	0.9	16.2	0.00	2.8	12.4	18.7
22-May-18	6.60	391	8.0	4.0	20.8	756.7	1	0.3	0.4	0.9	0.0	1.9	0.02	0.9	1.4	1.4
23-May-18	6.40	382	20.0	16.8	19.3	757.4	1	0.6	1.2	2.4	0.0	1.9	0.02	1.0	1.9	1.4
6-Jun-18	7.05	322	46.0	1.4	21.6	757.4	14	1.6	1.6	2.1	0.4	12.6	0.00	1.6	4.5	4.6
8-Jun-18	6.46	338	91.8	9.4	21.6	755.4	2	2.5	1.0	1.0	0.0	2.7	0.13	4.6	3.7	2.8
13-Jun-18	6.40	357	95.9	0.6	23.2	752.3	5	4.3	1.1	1.8	1.1	24.6	0.00	7.0	9.0	17.4
14-Jun-18	6.41	281	31.0	14.8	21.1	750.1	1	3.0	0.3	0.3	0.5	2.8	0.00	1.2	2.3	2.1
18-Jun-18	6.37	362	20.0	13.6	23.1	756.7	4	0.1	0.6	0.2	0.0	2.9	0.13	0.3	1.7	1.6
25-Jun-18	6.86	313	36.5	0.8	20.9	757.4	7	2.1	0.9	0.8	0.0	1.7	0.00	3.6	1.5	1.8
28-Jun-18	6.32	366	44.4	2.2	22.2	754.6	3	3.6	1.0	1.2	0.3	6.5	0.00	5.6	2.7	3.5
16-Jul-18	6.96	354	23.0	24.4	25.7	757.4	18	0.8	0.7	0.1	0.2	1.8	0.09	1.3	1.8	2.0
17-Jul-18	6.35	382	14.6	3.8	23.3	753.9	1	0.6	0.7	0.9	0.0	2.1	0.01	1.3	1.7	1.5
23-Jul-18	6.67	303	27.0	8.6	22.3	755.3	6	0.7	0.6	1.1	0.0	1.9	0.31	1.2	3.9	2.7
26-Jul-18	6.62	333	29.0	9.6	25.2	755.4	3	1.9	0.4	0.7	0.2	2.4	0.16	1.2	3.1	2.4

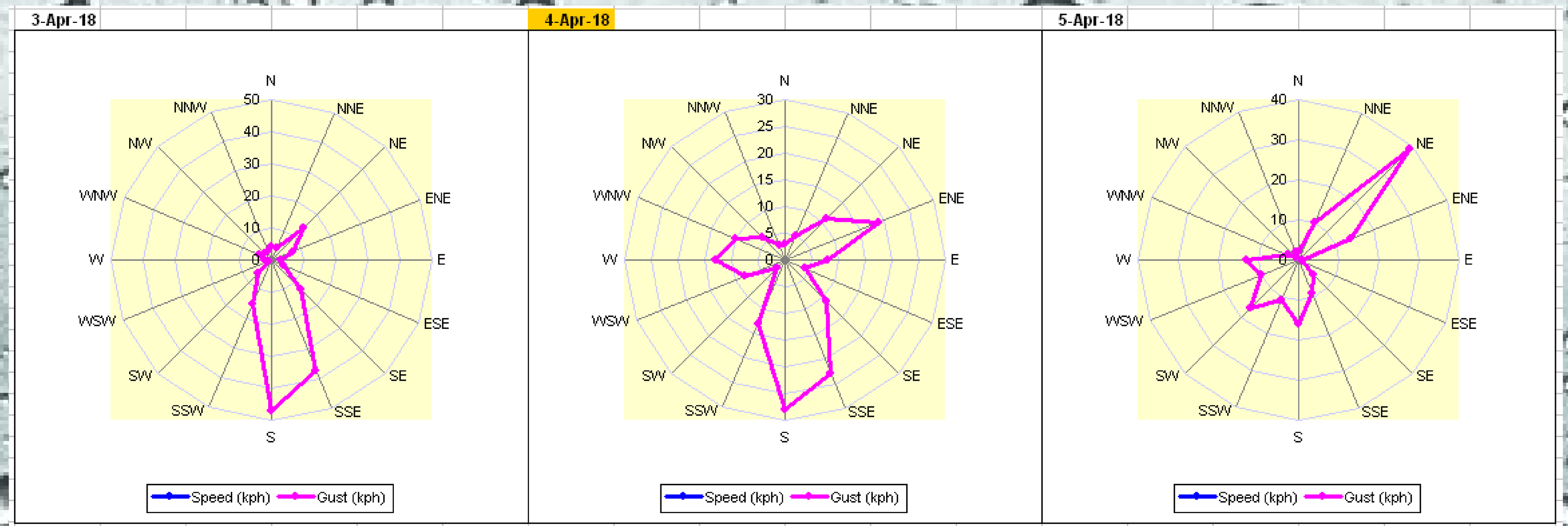

Fig.5, wind direction in the day before and after 4 April. Evident the west wind direction in the day of sampling

Discussions

The result of the chromatographic analysis showed that: comparing the sum of the concentrations (mili-equivalents/L) of the main cations (Na^+, K^+, NH_4^+, Ca^{++} and Mg^{++}) and the sum of the main anions' concentrations (F^-, Cl^-, NO_3^-, SO_4^{--}) it result, as was to be expected, a sufficiently linear trend (fig.2). An excellent correlation was found between the sum of the concentrations of sodium and potassium ions and that of chloride ion (fig.3). This suggests that these ions come mainly from seawater. The correlation between the sum of the concentrations of calcium and magnesium ions and that of the nitrate and sulphate ions (fig.4) could be caused by the neutralization process of nitric and sulphuric acids (coming from the nitrogen and sulphur oxides of anthropogenic origin), made only from calcium and magnesium carbonates contained in the dust derived from wind erosion.

The analysis of the rain's sample collected in April 4th (one of the day in colour of tab.1) showing that there is a high concentration of sodium and chloride ions in the rains and in the day of sampling, see fig.5, was a wind from west side of Tyrrhenian Sea and from south/ENE. On the contrary, it was found that, in the rain that fell on May 21st, high concentrations of calcium, nitrates and sulphates was present and that, in the previous day, it blew a wind from the north-east, fig.6, where there are calcareous mountains and industrial areas. Similar trend was on June 13th. All of those particular days, with high concentration of ions, compared with other, presents low amount of rain and in some case in the previous days did not rain at all, on the contrary in presence of strong wind and heavy rain probably the polluted gases and dust was removed, it way verified that cleaning effect which caused rain very poor of salts, as in 09 April and 08-09 of May. In 26 and 28 February it has fallen snow in Rome, but it's ion concentration is not different from the seasonal average.

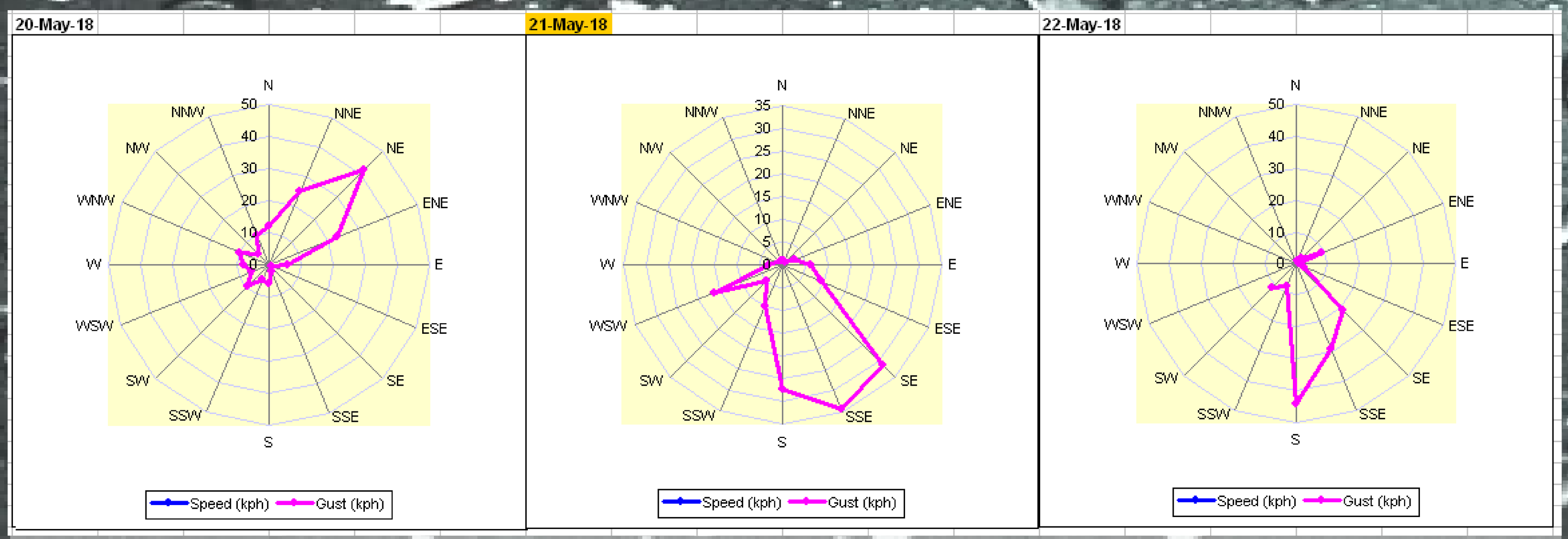

Fig.6, wind direction in the day before and after 21 May. Evident the SSE wind direction in the day of sampling

Exploratory data analysis

The principal components analysis (PCA) was carried out first on the whole data matrix with results not useful to separe among seasons. After a recalculation on the data using only the chemical-physical parameters, divided by seasons winter, spring and summer, pre-treating the data with autoscaling, but omitting the data of the ionic concentrations that turned out to be redundant for this purpose produce a visible separation.

The use of chemical-physical data alone has allowed the separation of samples between the different seasons with an explained variance of 68.4%. Scores have been reported in a 3D chart in fig.7

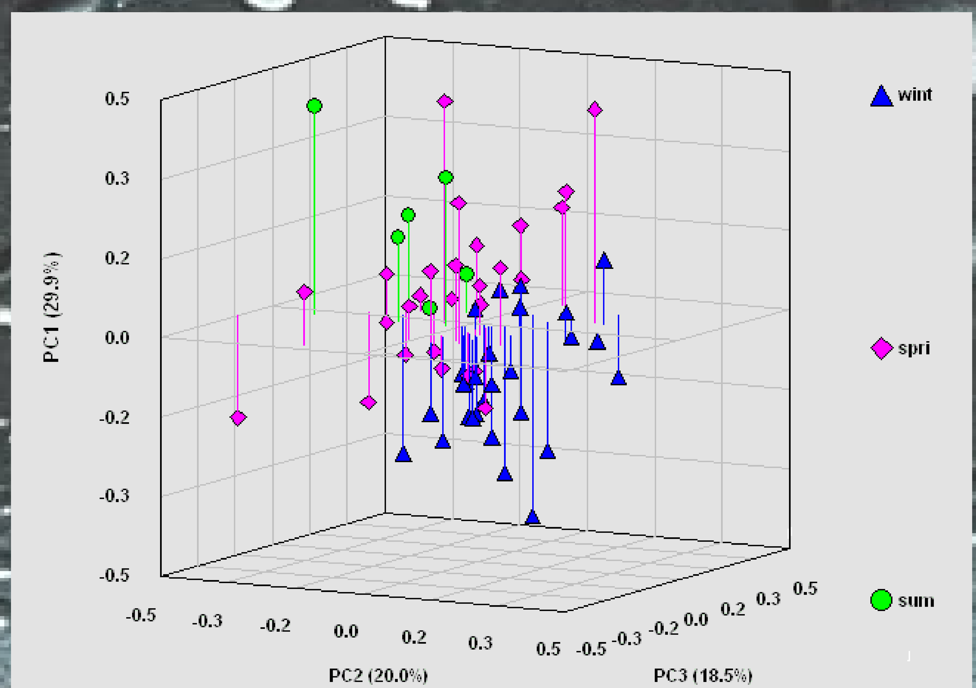

Fig.7, 3D graphic representation of the first 3 main components after dividing the data set of the rainfall in different seasons, using only the chemical-physical data and excluding the ionic concentrations

Conclusions

In conclusion, this research has shown that, even if there are no serious problems related to the acidity of the rain, there are in any case precipitation with a discrete content of nitrates and sulphates that can create problems for the numerous monuments and outdoor stone finds.

Also at certain times of the year there is a probable effect of transport of nitrate and sulphate from the industrial zone to the east of Rome and sea salt from the Tyrrhenian Sea to the west of Rome.

Finally, there is a certain degree of correlation between rainfall, pH, ORP and conductivity compared to the seasons. On the contrary, the trend of concentrations of the main ions seems to be independent of seasonal variations. We also hope the publication of data collected by various government agencies, to create a historical archive not only of rainfall, but also of its composition.

References

1) Mohsen S., Pejvak P.S., Acid Rain Examination and Chemical Composition of Atmospheric Precipitation in Tehran, Iran, Environment Asia, 2012, 5(1) 39-47
2) Cigna, A.A., Clemente, G.F., Giorcelli, F.G., On 134Cs in Rainwater from 1960 to 1969, Health Physics, 1971, 21(5) 667-672
3) Sanusi, A., Wortham H., Millet M., Mirabel P., Chemical composition of rainwater in Eastern France, Atmospheric Environment, 1996, 30(1) 59-71
4) Calvert, J. G., Glossary of atmospheric chemistry terms, Pure & Appl. Chem., 62(11). 1990, 2167-2219

XXVIII Congress of the Analytical Chemistry Division, 22 - 26 September 2019, Bari, Italy

For background we must thank Wallpaperscraft.com for "Drops Rain on Glass, n. 120628"