Bulk Atmospheric Deposition In An Urban And Rural Sites In The Southern Po Valley (Northern Italy)

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The atmosphere deposition influences the cycling of nutrients in eco and agroecosystems, contributing to the chemistry of plants, soils and surface waters.
The present work reports the pH and chemical composition of the rainfall bulk deposition at two sites in Italy, one in Bologna downtown and one in a rural site away from Bologna.
Efforts have been made to differentiate the degree of neutralisation and the seasonal trend of some ions. In addition, the two sampling points, located in two areas at different land use, have given us the possibility to determine the ions origins.

Methodology

The climate of the experimental sites is temperate-continental, with a mean temperature of 13°C and precipitation annual amount of 700 mm, rained mostly in spring and autumn.
The Site 1 (40 masl; 11° 28'; 44° 30' N) is located in the center city of Bologna (373,000 inhabitants), 80 km far from the Adriatic Sea. It is 50 m far from the nearest busy road (traffic density ≈ 10^3 vehicles per day) and the two main sources of domestic energy are gas oil (approximately 60%) and gas methane (approximately 40%).
The Site 2 (190 masl; 11° 29' E; 44° 25' N) is located in a rural area on the hills (calcareous soil) surrounding the town of Ozzano (5300 inhabitants). It is situated at a distance of 25 km from Bologna monitoring station. Agricultural fields and natural vegetation surround the Ozzano monitoring station. Wheat and barley are the main crops during the winter, while maize, sunflower and soybean are the main crops during the summer. The nearest industrial area is 6 km away towards the Northeast but two busy roads "Via Emilia" (10^3-10^4 vehicles per day) and "A14 highway" (10^4-10^5 vehicles per day) are in plain 2 km and 5 km.
Sampling of bulk deposition was carried out at the two sites by means of standard rain gauge. During the study period a number of 163 and 123 samples were collected at the Site 1 and 2, respectively.
On the day after collection, conductivity and pH (at 20°C) of samples were measured. Then a capillary electrophoresis system (Beckman P/ACE 5500) was used for the quantification of major anions (SO_4, Cl, NO_3, NO_2, PO_4, HCO_3) and cations (Ca, K, Mg, Na, NH_4), by the external standard calibration method with linear regression, according to the methods proposed by Dinelli et al**.** (1998).

Results

The weighted mean pH in the period of the three years was 5.1 in Bologna and 5.3 in Ozzano, with restricted fluctuation, ranging from 4.5 to 6.0 in Bologna and from 4.4 to 5.5 in Ozzano. The mean values fall within the pH range of the clean atmosphere, so this rainfall can not be define acid.
As it is evident in the table, the bulk deposition chemistry was dominated by three anions: SO_4^{2-}, NO_3^- and Cl^- .

Site	Cl	HCO_3	NO_2	NO_3	PO_4	SO_4	K	NH_4	Na	Mg	Ca	H
Bologna												
1997	22.26	7.04	1.52	27.32	0.73	30.12	8.03	7.43	11.09	0.17	12.71	0.05
1998	16.74	12.07	1.75	25.2	1.15	39.16	9.03	5.85	11.95	0.73	15.81	0.04
1999	35.66	9.52	2.51	31.03	2.21	44.34	9.52	7.77	21.02	2.14	20.27	0.06
MEAN	24.9	9.5	1.9	27.8	1.4	37.9	8.9	7.0	12.2	1.4	17.5	0.04
Ozzano												
1997	22.04	23.71	1.07	33.15	1.66	32.84	9.29	11.47	13.59	1.44	15.18	0.04
1998	17.93	23.20	1.10	36.23	0.58	32.31	4.21	9.29	12.19	1.36	20.25	0.04
1999	19.37	18.78	1.04	35.69	0.99	30.15	3.99	7.69	10.75	1.55	16.97	0.04
MEAN	19.8	21.9	1.1	35.0	1.1	31.8	5.8	9.5	14.7	1.0	16.3	0.05

Annual amount of anions (kg $ha^{-1}y^{-1}$) at the Bologna and Ozzano monitoring stations.

In Bologna and Ozzano the sum of SO_4^{2-}, NO_3^- and Cl^- volume weighted mean of their concentrations accounted respectively for 89% and 81% of the total determined anions, while Ca^{2+} and Na^+ were the two most abundant cations.
In the Bologna town the sulphates deposition increases significantly during the autumn-winter period. Probably, this is due to the residential heating, which constitutes, during the cold period, a local sulphure dioxide source, with elevate emission of that pollutant in the air.
Nevertheless in Ozzano SO_4 doesn't present a seasonal trend and its value remain similar to that one in Bologna during the spring-summer period all over the year.
Since, the rain pH depends on the chemical species present in the air and their relationships, the rainfall pH is maintained to normal value, despite the high concentration in the atmosphere of oxides of nitrogen and sulphates, thanks to the calcium presence in the air. This element arrives at our environment transported by the dust-rich wind of the Sahara desert during all the year. The other anions, taking part at the neutralisation of the main acidity, are hydrogenous and the ammonium.
Starting from the ions concentration in the rainwater, an index determines the acidity of rain with the following equation (Flues et al.,2002):

$$\text{Index} = \frac{S + N}{Ca}$$

where S, N and Ca are the sulphates, nitrates and calcium concentrations respectively, expressed in μeq l^{-1}. When this value is close to 1, the rainfall is not acid, despite the high concentration of acidic pollutant in the air.

Conclusions

Despite of the fact that our study sides are located in one of the most industrialized country in the world, pH values range from slightly acid to slightly alkaline. The chemistry composition of the bulk deposition can help to understand this: results show concentration of sulphates and nitrates, which are the main responsible for rainfall acidification, very elevate and in several cases higher then that ones surveyed in typical acid rain regions. The explanation of this apparent contradiction is in the study of the chemical reaction that takes part in the atmosphere. In particular, the presence of alkaline elements, principally the calcium, derived by the dust-wind from Sahara desert, neutralize the acid pollutants, keeping the pH to value typical of the clean atmosphere. That means that the rainfall pH can not be the only parameter to describe the atmosphere and rainfall quality. To obtain more specific and complete information, it is important an analysis of the contained ions. The presented index (S+N)/Ca can be used effectively to forecast the acidity of the rainfall. All the countries of the Mediterranean basin beneficiate of this phenomenon.
Annual mean deposition on soil of anions and cations can be ordered in a descending way as follows: SO_4>NO_3>Cl and Ca>Na in Bologna; NO_3 > SO_4>Cl and Ca>Na in Ozzano.
The different locations of the two sides, one in the Bologna downtown and the other in an urban area, help to understand the source of these ions. Thus, the anions differences can be ascribed to the different environmental and land use of the two sides: the higher amount of SO_4 in the town is due to the residential heating during the winter. In fact, the SO_4 has a predominant anthropogenic origin; the high nitrates deposition in both the sites is due to the proximity to trafficked roads and the prevalent wind direction in the case of the site in the rural area. In Ozzano we found also an elevate concentration of ammonium due to fertilizers applications in agricultural fields. This ion is present in lower concentration in Bologna town.
These results indicate that the principle sources of pollution are local: fossil fuel combustions, heating and fertilizers.
The other ions present in the atmosphere derive principally from seawater or are crustal element.

References

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