AN APPLICATION OF MULTIVARIATE ANALYSIS TO ACID RAIN DATA IN NORTHERN ITALY TO DISCRIMINATE NATURAL AND MAN-MADE COMPOUNDS

GIOVANNA FINZI
Centro Teoria dei Sistemi CNR, Dipartimento di Elettronica, Politecnico di Milano, Italy

ALBERTO NOVO
ENEL Centro Ricerca Termica e Nucleare, Milano, Italy

and

SILVIO VIARENGO
METIS Srl, Torino, Italy

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Abstract. This paper presents the preliminary results of a study, the aim of which was to analyse the pluviometric and chemical rain data, recorded by a wet only network located in Northern Italy. More in detail, precipitations were collected on a weekly basis and chemical analysis was performed on pH, electric conductivity and Ca, Mg, Na, K, NH₄, NO₃, SO₄, Cl concentrations.

The Principal Components Analysis pointed out that the first three components are enough to explain more than 90% of the variability of the parameters. Moreover each component may have a different physical interpretation, that is the first one is mainly related to the precipitation amount, while the second to the man made and natural sources and the last one to the sea/soil contribution.

Introduction

Acid precipitation is at present one of the most complex problems that environmental researchers have been dealing with during the last ten years. In fact, in addition to the difficulty in identifying the chemical reactions leading to the formation of acid compounds in the atmosphere, it is even more difficult to identify the pollution sources which caused the phenomenon.

Pollutants may be transported for thousands of miles over many days before their deposition takes place. Sulphur and nitrogen oxides, in particular, may accumulate in the atmosphere and give rise to acid compounds affecting the terrestrial ecosystem in many different ways, either directly or indirectly through, for instance, the corrosion of materials, the deterioration of monuments and the decline of forests.

According to the different sources, the chemical composition of acid precipitations changes in terms of the ion species which can be detected through the analysis of the rain samples. Generally speaking, three main different origins can be distinguished as follows:

- An anthropic source (of urban, industrial or agricultural type).
- In this case, sulphates and nitrates together with high acidity can be ascribed to an urban or industrial prevailing contribution, while high values of ammonium point to an agricultural source.
- A terrestrial source, which gives a prevailing contribution in terms of calcium, magnesium and potassium, due to the transport of particulate matter lifted from soils, unpaved roads or desert lands.
- A sea source, mainly connected to the presence in sea water of sodium and chloride ions together with a minor amount of magnesium and sulphate.

In this paper, the results of a multivariate statistical analysis performed on precipitation data recorded in Northern Italy will be shown. More specifically, two measurement stations were chosen, one in the city of Milan, representative of an urban precipitation quality, and one in Alpe Gera, located in the Aips at an elevation of 2100 m.

The aim of this study is to quantify the existing relationships among some of the ionic species in acid precipitation by means of a cross correlation analysis and to try to discriminate between the different sources of pollution by examining the results of a principal components analysis on the data.

The Data Set Collection and Handling

During 1983–84 a precipitation quality measurement network was built and run in Northern Italy through the cooperation of various institutions (Gruppo di Studio, 1987). In subsequent years, ENEL (the Italian National Electricity Board) extended its own network to the entire Italian area in collaboration with the Ministry of Agriculture and Forestry (Figure 1).

Moreover, the samplers have been changed from the preceding bulk type to the present wet-dry instruments (Novo et al., 1988) which allow for the discrimination between wet and dry depositions. Unfortunately, the two different sampling methods produce measures which are hardly comparable; this is the main reason why the following analysis was performed solely on data recorded by the second kind of instruments, starting from 1986. Furthermore, the samples are collected on a weekly basis, so that they are representative of all the precipitation events over a seven days period.

The two stations examined in this study are shown in Figure 1. The first station is located in the centre of Milan, a highly populated city (~ 2000000 inhabitants), where there is often severe atmospheric pollution mainly due to domestic heating and traffic. The second station is located at the base of the Bernina glacier, at Alpe Gera (2100 m elevation), in an uncontaminated mountain site, far from any significant urban or industrial area.

Each weekly sample was analyzed for its main chemical constituents, and thus the data base reports the following ionic contents: H\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Na\(^+\), NH\(_4\)\(^+\), SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), HCO\(_3^-\), which all have the units mg/l.

The last compound (HCO\(_3^-\)) was not considered in the statistical analysis, because the values were always negligible, due to the prevailing acidity (pH < 5.6) of the water samples. The potassium data were also not taken into account, because of low values due to the scarce recycling of potassium from soils and wood combustion.

Statistical techniques used in the analysis include cross correlation and principal components.