

## AIR POLLUTION IN SANTIAGO (CHILE) AS STUDIED BY NUCLEAR AND OTHER TECHNIQUES

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### Abstract

Santiago, the capital of Chile is becoming one of the most polluted cities in the world as regards its atmospheric environment. The present project aims at comparing the composition of airborne particulate matter collected in Santiago with other collected in a clean area and to optimize the analytical methodology, based on NAA, XRF and PIXE, for this type of samples. The possibility of using total reflection XRF (TRXRF) for quantitative determination of air particulate matter will be evaluated. Analysis of wet deposition by ion chromatography and TRXRF will also be performed. The feasibility of using biomonitors for environmental pollution purposes will also be studied. The project foresees the evaluation of the analytical data as regards its analytical quality and its statistical interpretation. The identification of emission sources will be attempted.

### 1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Santiago, the capital of Chile has relatively high levels of pollutants as compared to other large cities in the world as regards its atmospheric environment. The large number of motor vehicles, for public transportation and private use, the large number of industries located within urban limits and adverse topographical and climatic conditions, contribute to the high levels of airborne particulate matter and gases found in the atmosphere of Santiago.

The natural climatic and environmental surroundings of Santiago contributes very little to a natural cleaning of the city's air. The city is located in the central region of the continental part of the country, at an altitude of 543 m above sea level, at a latitude of 33° 30' south and a longitude of 70° 35' west. It covers an area of 144 km<sup>2</sup>, (Fig. 1) has a population of about 5,000,000 inhabitants and around 500,000 vehicles. The mean temperature in winter is 9 °C and in summer is 23 °C. The rain season coincides with the winter season, that is, from May to August. The mean rain fall in the last five years was about 384 mm. Santiago is almost completely surrounded by mountains: at the east the Andes Mountain (ca. 2000 to 4000 m altitude) and at the west the Coastal chain mountain (ca. 800 to 1000 m altitude), which are connected by transversal chains of low altitude.

The winds regime is also adverse. The highest wind velocities, with a value of about 5.0 m/s, are produced during the summer season, while the lowest velocity, with

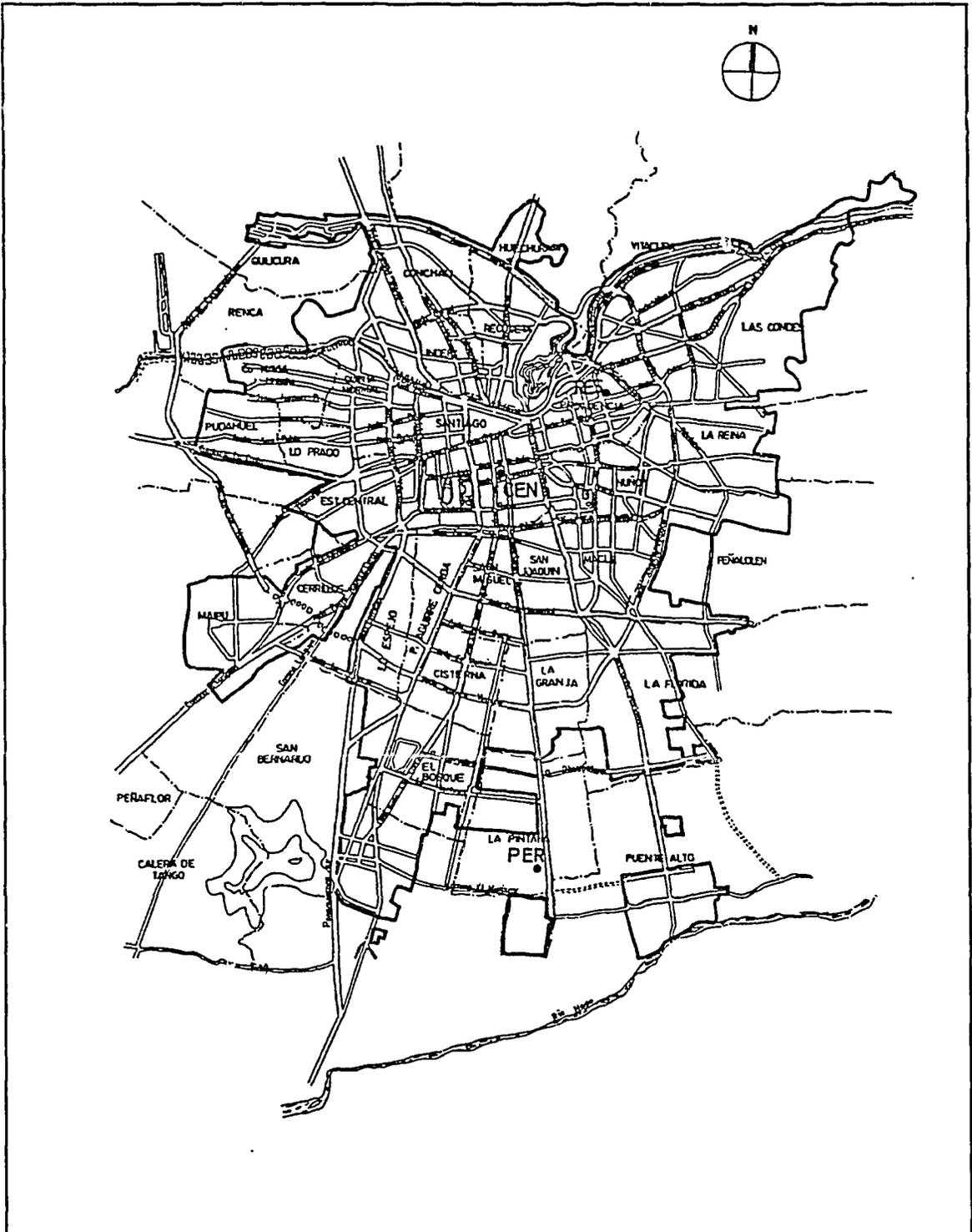


Figure 1. Map of Santiago, Chile

values as low as 0.6 m/s, occurs during the winter season. The mean yearly value could be between 1.0 to 1.2 m/s. This fact shows how important the heating process by solar radiation is as compared with the circulation of air around the Santiago area. The higher wind velocities coincide with the period of major solar radiation. The winter months, with lower solar radiation and smoggy days have a daily cycle of winds with very small changes. The south-west wind direction is the predominant in Summer with a 56% of occurrence, followed in importance by the south and west direction. Furthermore, in winter months only the south-west wind direction is relevant with an occurrence of about 28% followed by the east direction with a 19% occurrence. Table I shows a typical wind behaviour in the Santiago area for the period September 1982 to August 1983 [1].

TABLE I. WIND VELOCITIES IN SANTIAGO, CHILE, FROM SEPTEMBER 1982 TO AUGUST 1983. VALUES IN m/s.

	Summer	Autumn	Winter	Spring	Year
High value	5.0	3.6	2.7	4.1	4.1
Lower value	0.9	0.7	0.6	0.9	0.9
Mean value	2.3	1.5	1.4	2.0	1.8

The four seasons of the year are clearly distinguishable. The worst period, as regards air pollution, is winter, from May to August. During this period a thermal inversion layer is produced at around 300 m above the city which greatly contributes to the accumulation of pollutants in Santiago's atmosphere. This inversion layer normally breaks up at around midday, but it is not enough to disperse all pollutants. The cycle is then repeated next day.

Industries are spread at the south and north of the city in the pathway of the winds. Thus, in the daytime, when the wind blows from the south-west, all the industrial emissions from that sector are blown into the city. On the other hand, at night something similar happens from the northern industrial area.

The direct consequence of this problem is the large number of persons, especially children, with respiratory difficulties, eye irritation and allergies. This fact has a marked effect on the production, labour and attendance of children to school.

The local authorities have given to this problem high priority and are enforcing new measurements to decrease the air pollution in Santiago. One of the latest regulations is the introduction of catalytic converters in all types of new cars aiming at decreasing the levels of toxic gases. The industries have to revise all their emission systems and to install adequate emission control devices or filters.

There have been a number of studies on air pollution in Santiago. The results of these studies indicate that airborne particulate matter is an important component of Santiago atmosphere. There have been attempts to characterize the aerosol, but the results have not been very successful. Most of the analytical techniques used so far have been destructive methods of analysis which required rather complicated sample preparation procedures. One study, which used a purely instrumental approach, namely instrumental neutron activation analysis (INAA) was carried out in 1977 [2]. At present, several analytical techniques are available, namely neutron activation analysis (NAA), x-ray fluorescence (XRF) [3,4] proton induced x-ray emission (PIXE), which can be used to characterize the aerosols.

The present project aims at:

1. to compare the composition of airborne particulate matter collected in Santiago with other collected in a clean area; for this purpose, a non-polluted sampling site has been selected at about 30 km from Santiago
2. to optimize the analytical methodology, based on NAA, XRF and PIXE, for this type of samples. The possibility of using total reflection XRF (TRXRF) for quantitative determination of air particulate matter will be evaluated [5,6,7]. A TRXRF system is available at the Chilean Nuclear Energy Commission and two approaches will be explored:
  - a) the analysis of airborne particulate matter collected directly on quartz plates for direct measurement and
  - b) the collection of samples on membrane filters followed by a chemical dissolution and subsequent analysis of the solution obtained
3. analysis of wet deposition by ion chromatography and TRXRF; this part will be included in the supplementary programme
4. to study the feasibility of using biomonitors for environmental pollution studies in both, the Metropolitan and rural areas will also be explored
5. to evaluate the analytical data as regards its analytical quality and to treat it statistically; the identification of sources will be attempted.

## **2. MATERIALS AND METHODS**

### **2.1. Sampling and sample preparation**

The collection of airborne particulate matter in Santiago and rural area will be carried out using a sample collector which complies with the PM-10 standard provided by the IAEA.

Two samples will be collected on a daily basis, one during the daytime and the second overnight, ideally simultaneously at both collection sites. This is, however, subject to the availability of a second PM-10 sampler which is expected to be obtained through an IAEA Regional Programme on Environmental Studies Using Nuclear Techniques (RLA/2/006)

For the analysis of the filters with instrumental analytical techniques, the samples will be analysed directly, without any further treatment. The best analytical conditions for each technique will be determined experimentally. Those samples to be analysed by TRXRF have to go through a dissolution process. The most appropriate procedure will be determined experimentally.

For the collection of wet deposition it is foreseen a co-operation with the local meteorological organization which has the appropriate sampling devices.

## **2.2. Analytical techniques**

The analytical techniques for the analysis of airborne particulate matter collected onto filters will be NAA, XRF and PIXE, complemented if necessary, with classical methods such as atomic absorption spectrometry (AAS). The analysis of wet deposition, as part of the supplementary programme, will be done by ion chromatography and electrochemical methods in addition to NAA and TRXRF.

The respective analytical methodologies, with the exception of TRXRF, are already developed. However, it might be necessary to optimize some of the parameters to obtain more reliable results. For TRXRF it will be necessary to develop the complete analytical procedure since this technique has only recently been introduced and there is no experience for the analysis of airborne particulate matter. In addition to the development of sampling procedures, it will be necessary to determine the best chemical approach for the complete dissolution of the sample and subsequent steps. The optimum parameters (irradiation, geometry and counting conditions) will be determined.

## **2.3. Analytical quality assessment**

Due to the lack of appropriate reference materials for this type of matrix, analytical quality control will be based, mainly, in the exchange of samples among the local participating laboratories for cross checking the results. For this purpose, it is planned to collect two samples simultaneously, at the same collection site during the same time with two identical samplers. The filters will then be analysed by two independent methods and the results compared.

It would be highly desirable to have some kind of reference materials prepared for this CRP. Previous experience of the IAEA on the subject can be taken into account and attempt the preparation of such materials.

## 2.4. Data evaluation

The analytical data will be interpreted in several ways. On one hand, enrichment coefficient will be calculated for all elements with respect to the concentration of those elements in the earth crust. This will allow the identification of natural and anthropogenic elements. On the other hand, the data obtained from the samples collected in Santiago and the rural site will be subject to statistical analysis to determine significant differences or similarities among these collection centres. Finally, the data will be used to check the validity of diffusion models which are being developed by another group; the elemental composition of the aerosols could provide valuable information for this purpose.

## 3. RESULTS

No results have been obtained so far within the framework of this CRP. However, the air pollution problem in Santiago is not new and has been studied before. However, further studies have to be undertaken to help in identifying the actual pollutant sources, mainly the static ones.

One of such studies was the "Physical and Chemical Characterization of Atmospheric Aerosols in Santiago" [1] which was carried out from 1983-1987 with the sponsorship of the Ministry of Health of the Government of Chile and with the participation of academic groups from three Faculties of the Universidad de Chile. The elemental composition (Cu, Ti, Pb, Mg, Ca, V, Zn, Fe, Ni) and some compounds (sulphate, nitrate, halogenate) were determined in the aerosol samples. This study included the analysis of a lot of filters (Whatman GFA) collected on high-vol samplers during the previous two or three years. Only a few of them were especially collected on dichotomous samplers for some determinations. Other objective of this study was to attempt to determine the origin of some of the compounds found in the samples.

Tables II and III show some of the results obtained in the analysis of samples collected in Santiago between November 1976 and July 1983 [1].

TABLE II. AIRBORNE PARTICULATE MATTER AS DETERMINED IN ATMOSPHERIC AEROSOLS FROM SANTIAGO (CHILE). VALUES IN  $\mu\text{g}/\text{m}^3$

	Summer	Autumn	Winter	Spring	Year
High value	331	479	566	355	566
Lower value	80	93	72	57	57
Mean value	184	250	287	175	232
Number of event	86	126	166	132	510

TABLE III. ELEMENTAL AND IONIC COMPOSITION  
OF ATMOSPHERIC AEROSOLS IN SANTIAGO, CHILE.  
VALUES IN  $\mu\text{g}/\text{m}^3$

	Summer	Autumn	Winter	Spring
Fe	1.112	1.432	1.726	1.225
Pb	0.206	0.348	0.496	0.188
Cu	0.078	0.083	0.046	0.075
Mn	0.194	0.203	0.058	0.232
Ni	0.020	0.025	0.034	0.022
Ca	0.790	0.128	0.088	0.082
Mg	0.320	0.318	0.226	0.210
V	0.020	0.015	0.038	0.015
Ti	0.086	0.112	0.876	0.095
Al	0.794	0.430	0.030	0.607
C	23.32	43.85	143.41	20.30
SO <sub>4</sub> <sup>2-</sup>	10.27	11.69	17.34	10.91
S	5.14	7.00	11.15	6.16
NO <sub>3</sub>	5.99	6.83	12.35	4.98
NH <sub>4</sub> <sup>+</sup>	0.57	0.86	1.21	0.60
X*	3.88	3.59	3.57	3.56

\*X = total halides

International support for related studies has been obtained. One such study is being carried out within the framework of a Regional Programme on Environmental Studies using Nuclear Analytical Techniques, RLA/2/006, sponsored by the International Atomic Energy Agency. This international co-operation project includes the analysis of atmospheric aerosols of Santiago and its seasonal variations. The analysis of the samples is being done with nuclear (*i.e.* NAA, PIXE, isotopic dilution) and classical analytical techniques (*i.e.* AAS, ion chromatography). The samples are being collected with SFU and PM-10 equipment. The principal objective of this project is to study the seasonal characterization of these aerosols and to compare it with the incoming particulate matter into the city. A mass balance estimation for all the chemical species is another interesting objective of this study. This project is being carried out with the participation of a group of scientific staff of the Universidad de Chile and the Comision Chilena de Energia Nuclear.

#### 4. PLANS FOR FUTURE WORK

The work plan, within the "core" programme for the proposed CRP would include the following:

1. An elemental characterization of the urban aerosol in Santiago using different non-destructive analytical techniques such as NAA and XRF. As a complement it is also proposed to use AAS for selected samples. A suitable "clean" area will be identified to be used for comparison purposes.
2. Emphasis will be put on analytical quality control to assure adequate quality of the analytical data, which would be the basis for any interpretation that could be carried out. Quality control would be done through analytical intercomparison of duplicate samples analysed by several of the analytical techniques available, analyzing appropriate reference materials and through the exchange of samples with other national or international institutes dealing with the same subject.

As part of the supplementary programme it is planned to analyse wet deposition in the Santiago metropolitan area. Studies of this kind have not been undertaken so far. The total reflection mode of XRF is available at the Chilean Nuclear Energy Commission, La Reina Nuclear Centre. It is proposed to implement and develop the necessary procedures for its use in the analysis of wet deposition and any other matrix for which these techniques have proven to be useful and reliable and relevant to this project. An attempt to find suitable biomonitors for environmental pollution in the city itself and mainly in the suburban area, will also be carried out. This component of the supplementary programme is not well defined and decided yet.

During the first year the activities will be focused on the selection of the collection sites, improvement of the analytical procedure for the elemental characterization of atmospheric aerosols samples collected on filters or membranes and the development of procedures for the use of total reflection XRF for the analysis of aerosols and wet deposition.

## REFERENCES

- [1] UNIVERSIDAD DE CHILE, Estudio de Caracterización Física y Química de Partículas en Suspensión en la Región Metropolitana (Study on the Physical and Chemical Characterization of Airborne Particulate Matter in the Metropolitan Area), Report, University of Chile, Santiago, Chile (1985).
- [2] ANDONIE, O., ORTIZ, J., Análisis de los Aerosoles Atmosféricos de la Ciudad de Santiago Mediante Análisis por Activación Neutrónica (Analysis of the Atmospheric Aerosols of Santiago Using Neutron Activation Analysis), Thesis, University of Chile (1977).
- [3] WOBRAUSCHEK, P., KREGSAMER, P., STRELI CH., ALGINGER, H., Recent developments and results in total reflection X-ray fluorescence analysis, *Advance in X-ray Analysis* (C.S. BARRET, Eds) Vol. 34, Plenum Press, New York (1991).
- [4] KLOCKENKÄMPER, R., VON BOHLEN, A., Total reflection X-ray fluorescence: an efficient method for micro, trace and surface layer analysis, *J. Anal. Atomic Spect.* 7 (1992) 273-279.

- [5] MICHAELIS, W., PRANGUE, A., Trace analysis of geological and environmental samples by total-reflection X-ray fluorescence spectrometry, Nucl. Geophys. **2**(4) (1988) 231-245.
- [6] LELAND, D.J., BILBREY, D.B., LEYDEN, D.E., WOBRAUSCHEK, P., AIGINGER, H., PUXBAUM, H., Analysis of aerosols using total reflection X-ray spectrometry, Analytical Chemistry **59** (1987) 1911.
- [7] KETELSEN, P., KNÖCHEL, A., Multielementanalyse von Aerosolen mit Hilfe der Röntgenfluoreszenzanalyse mit totalreflektierendem Probenträger (TRFA), Fresenius Z. Anal. Chem. **317** (1984) 333-342.