STUDY OF AIR POLLUTION IN BUENOS AIRES CITY USING NEUTRON ACTIVATION ANALYSIS AND X-RAY FLUORESCENCE

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Abstract

Buenos Aires city and its surroundings, has a huge population and very dense traffic. There are many possible pollution sources that can be identified, but other characteristics such as weather and location counteract some of these sources to the benefit of the atmosphere of the city. Although several groups have been working on these subjects, there is not enough information about which elements are present in Buenos Aires air. The aim of this project is to provide information about the elemental profile of the atmosphere of the city and to evaluate and to make an interpretation of the obtained data. Both XRF and INAA are going to be used for analyzing the air filter samples with the participation of the Meteorological Service in sampling and interpretation of the results. By choosing adequate sampling sites and times, differences between day/night, week day/weekend will be looked for. The influence of non-leaded petrols will be studied. Some work on air samples was done before the beginning of this contract to settle future working conditions. Some results from this study are presented only as preliminary ones. Sampling will begin during this April at two sites with different traffic density. For both XRF and NAA suitable standards will be prepared. Medium and long lived nuclides are going to be analyzed by INAA. Plans for 1993 are given as well as possible collaboration with other groups in the country.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

1.1. Introduction

Argentina is a South American country of approximately 2,800,000 square kilometres with a population of 35 million inhabitants. The federal capital is Buenos Aires and is located at 34°38' S, 53°29' W, by the Rio de la Plata river, it has a surface of 200 square kilometres and a population of about 4 million habitants. The Great Buenos Aires belt which comprises 19 municipalities, surrounded the city, forming the Buenos Aires Metropolitan area. This area covers 3800 square kilometres and holds a population of more than 11 million people. From now on, all the mentions to Buenos Aires will be referring to the Buenos Aires Metropolitan area (Buenos Aires city plus Great Buenos Aires).

Vehicle combustion exhausts must be taken into account as the principal cause of deterioration of the atmosphere of the city. Vehicle circulation has been estimated in 1,700,000 cars, 40,000 taxis and 10,000 buses plus an uncertain number of trucks not evaluated at this census (1991). Buenos Aires has a very dense public transportation network mostly based on buses. Most of them have diesel-motors which produce dense dark smokes, principally due to poor combustion conditions. Although the use of natural gas has become popular, especially among taxi owners, the vast majority uses leaded petrol. The non-leaded type has begun to be sold only since the second half of 1992.

Although Buenos Aires cannot be considered as an industrial city, there are a great number of industries within its limits. The existence of a big harbour and the confluence of all the national transportation network, were the principal causes for the settling of all kind of industries. After the Second World War the relative percentage of industries in the city diminished due to the explosive growing of the Great Buenos Aires. This can be divided into two rings, a first one by the city limits, heavily industrialized and an outer one with industries and small agricultural areas.

In fact there exists an industrial corridor, more or less parallel to the rivers Parana-Rio de la Plata, running from Zarate (90 km N from Buenos Aires, 65,000 inhabitants) to La Plata (56 km S from B.A., population 450,000). More than 40 % of the national industry is located here; towards the north there are siderurgy, car, electronics, metallurgy, chemical, pharmaceutical and plastic plants. To the south, in addition to several of these industries there are important leather, fur and meat processing plants, distilleries and soap and detergent producing factories. Near La Plata there's a big distillery (32 % of national petrol processed here), a petrochemical complex and a siderurgy plant.

During the 1970's several laws prohibited new industry settlements within the city limits plus a ring of 60 km around it and contemplated the relocation of certain type of industries considered as highly polluting. In 1983 Municipal authorities approved the Environmental Prevention Pollution Code, and a policy of tax reduction was begun in order to encourage the location of industries in other provinces of the country.

Industries must undergo an official census but there are a lot of undeclared ones so it is very difficult to have an accurate inventory and control of their processes and effluents. From some months now, the authorities have been performing control operations over some industries, mainly as a consequence of denounces and as a part of a growing campaign of both inhabitants and authorities, interested in life quality and environmental preservation.

Another source of pollution are the thermal power stations which consume fuel-oil during winter months. The rest of the year they use natural gas. There is a project, starting this year, between the International Co-operation Agency of Japan and the Argentine Secretary of Energy and the Atomic Energy Commission for the study on air pollution control in Argentine thermoelectric central.

With respect to pollution arising from domestic uses, this contribution is not very important, since natural gas is mostly used for cooking and heating and private refuse incineration was prohibited some years ago. Sedimentary dust and suspended particles, from different origins are important factors of deterioration of the atmosphere, especially at Great Buenos Aires.

Since the early 1970's different agencies, either national, provincial or municipal have been dealing with partial aspects of environmental problems. Until the early 1980's, there existed an air sampling network for the capital, run by the Municipality (Secretary of Environment and Urban Planning) consisting of 12 stations for the evaluation of daily amounts of nitrogen oxides, carbon monoxide and sulphur dioxide and less frequently, volatile organic compounds, lead, smokes, sedimentary dust and suspended particles. But nowadays there is only one reference sampling station which continues to determine trends.

A report from the Laboratory of Atmospheric Surveillance, depending of the above mentioned Secretary, indicates an increasing trend for the last five years, for carbon monoxide and nitrogen oxides concentrations, although the annual statistical averages are still below the accepted values (Environmental Pollution Prevention Code, CO: 15 mg/m^3; nitrogen oxides: 0.4 mg/m^3). For sulphur dioxide, the annual averages don't show any trend and are significantly lower than the accepted limit of 0.5 mg/m^3. This has been related to the generalized gas use instead of other combustibles and the low sulphur content of Argentine oils. The values for sedimentable dust, suspended particles and smokes are higher than the limits of the Code and they strongly depend on the sampling site.

For lead there are contradictory values. In the municipal report, it is claimed that lead concentrations are lower than the maximum accepted values of 1 $\mu g/m^3$ but in the work of Caridi *et al.* [1], the values are significantly higher depending on the sampling site (downtown, day, high density of traffic, 3.9 $\mu g/m^3$).

With respect to other trace elements, there is no information, unless the studies originated to denounce certain industries as being polluting.

But Buenos Aires has the advantage of being located on a very wide plain, being the highest point of the city only about 30 m a.s.l.. This situation and the proximity of the river explains a ventilation that reduces pollution effects. This beneficial action is somehow diminished downtown (financial district) because although this area is located by the river, a compact sector of high buildings acts as a barrier. The humid clime of Buenos Aires is strongly influenced by winds; the cold and humid winds from the South Atlantic cause weeks of rain and stable temperatures, and the fresh and dry winds from the SW cause sudden changes of weather, usually after a long period of North wind (tropical hot air). Meteorological inversions seldom occur during high pressure winter conditions, when the accumulation of pollutants over the city can clearly be seen. These

inversions are destroyed by the changing meteorological situation and rarely last more than two or three days, but this is merely a good influence and it has not been quantified yet.

This introduction gives an overview of the factors that can affect Buenos Aires atmosphere. Although the city does not have the pollution problems of other ones of comparable size and population, the study and control of toxic or potentially toxic substances in its atmosphere has not received the attention that the problem deserves. In spite of the quantity of working groups and institutions having to do with pollution subjects, no studies have been performed on the quality of the city atmosphere in connection with its trace element concentrations.

The aim of this project is to study air filter samples of Buenos Aires by both Instrumental Neutron Activation Analysis (INAA) and X-Ray Fluorescence (XRF) and thus providing concentration values for elements present in the atmosphere. It is not intended as an overall control or measuring programme, but as a preliminary study which could call the attention of the authorities and of other Argentine researchers about the importance of this subject.

1.2. Work already done on the subject

During the last months of 1990 the NAA laboratory of the Argentine Atomic Energy Commission, got in contact with the Air Pollution Centre of the Meteorological Service and conversations began about collaboration in the analysis of samples related to atmospheric pollution, especially air filter samples. The Air Pollution Centre had been working on atmospheric aerosols, rain events and atmospheric precipitation studies.

Along the two following years and in different occasions, the Centre provided air filter samples to the NAA group. As some of them were in some way damaged from manipulation or had been used for electronic microscopy studies, they were used to settle conditions for future irradiation and counting schemes. Some of the samples were from Pennsylvania (Pennsylvania State University) and others from Buenos Aires Central Meteorological Observatory, a park in a residential area at the highest point of the city.

These Buenos Aires samples had been originally taken for a study of particle size and number distribution by electronic microscopy and the organic qualitative composition was characterized [2]. The sampling was performed with stacked filter units, using Nuclepore filters on open front filter holders and following two possible pore size combination schemes: 8, 3, 0.4, 0.2 μm and 3, 0.4 μm. Air mass stability conditions were selected as a pre-requisite for sampling since filtering was used for sampling periods from 12 to 24 hours.

The first irradiations for INAA were carried out at the RA-3 reactor of the National Atomic Energy Commission, to study the effect of irradiation time and position on both filters and containers. Quartz ampoules and several types of plastic vials were tried. Difficulties arose on many occasions due to reactor changes of its operating power. These

early tests didn't include standards, but qualitative analysis showed the necessity of changing the sample into a fresh vial, once irradiated. Practice in manipulating filters prior to irradiation was gained and decay time and measuring conditions were also adjusted.

While these experiences were carried out, a new irradiation position behind the graphite reflector was opened. After some tests were repeated, it was decided to use this position for future irradiations.

Once an analyzing scheme was set, some Buenos Aires samples were irradiated along with the IAEA standard Soil 7 to obtain some quantitative preliminary results by INAA. Among these samples, three had been taken using only one filter (0.4μm).

On February, another irradiation facility (RA-1 reactor CNEA) became available so some experiences to set irradiation conditions are being done now.

2. METHODS

2.1. Sampling

A sampling campaign is beginning in April 1993. Twelve hour sampling will be used downtown, to allow discrimination between day and night. At certain sites, 24 hour sampling will be preferred.

Two sampling sites with different traffic densities, have been selected to begin with, downtown, at a very busy financial and commercial area and at a residential neighbourhood. A third site may be included simultaneously with the above mentioned two. Although during the next months sampling sites may be changed and even its number increased, the scheme of different traffic density areas will be kept.

Sampling will be carried out using the stacked filter unit sent by IAEA and another set of pump plus open front filter holder, from CNEA. The Meteorological Service will be collaborating with a third equipment on some occasions. Nuclepore filters will be used.

2.2. Analytical Methods

The samples will be analyzed first by XRF and then by INAA. Filters will be weighed prior to and after sampling, with a 24 hour acclimatization to the balance room conditions [3].

Dispersive wavelength XRF will be done for both light and heavy elements, giving special attention to lead and suitable standards will be developed for quantitation.

For INAA, two irradiation facilities are available; the RA-3 reactor (Ezeiza Atomic Centre, CNEA) of 4,5 MW and a thermal flux of $3 \cdot 10^{13}\, n \cdot cm^{-2} \cdot s^{-1}$ and the RA-1 reactor

(Constituyentes Atomic Centre, CNEA) of 40 kW and a thermal flux of 10^{12} n·cm^{-2}.s^{-1}. The INAA laboratories are located at the Ezeiza Atomic Centre.

Irradiations will be mostly done at RA-3 reactor, for 6 h. Once irradiated, the samples will be transferred to fresh vials for their measurement.

As there is no pneumatic facility available, it is impossible to determine short-lived nuclides. Medium- and long-lived ones will be measured after a 7 day and an approximately 3 week decay respectively. For gamma spectrometry, two detectors will be used, a hyperpure Ge one, 1.9 keV resolution (for 1332.5 keV Co-60 peak) and a Ge(Li) of 2.2 keV resolution, coupled to a Series 85 Canberra multichannel analyzer. The spectra will be processed with a software developed at the laboratory.

Standards are going to be prepared at the laboratory and they will be checked against certified materials. For quality assurance, certified reference materials will be used to test the accuracy and precision of the analytical method, along with each spectrum individual evaluation and the participation in future interlaboratory comparison rounds.

With respect to data evaluation, the Statgraphics program will be used as a first step and enrichment factor calculations will be done. The Meteorological Service will participate in the data interpretation.

3. RESULTS

To illustrate what was observed and quantified in Buenos Aires samples, some of the obtained concentration values are given. For those samples coming from a scheme of three filters of different pore size, most of the concentration values were not of good quality. The results shown in Table I are for 12 h samples taken on Nuclepore 0.4 μm as a unique filter. The three samples are from residential areas, but sample 3 is from a higher

TABLE I. ELEMENT CONCENTRATIONS IN AIR FILTER SAMPLES OF BUENOS AIRES.
Values in μg per 1 g of sample

	Sample 1	Sample 2	Sample 3
Br	0.931 ± 0.058	0.841 ± 0.050	0.270 ± 0.040
Co	----	0.008 ± 0.002	----
Cr	0.102 ± 0.021	0.103 ± 0.021	0.221 ± 0.029
Fe	7.79 ± 0.93	9.7 ± 1.2	4.73 ± 0.86
La	0.0044 ± 0.0006	0.0094 ± 0.001	0.0037 ± 0.0007
Na	2.79 ± 0.10	10.03 ± 0.20	11.5 ± 1.2
Sm	0.0063 ± 0.0001	0.0010 ± 0.0001	0.0061 ± 0.0001

traffic density one. Results are expressed in μg per 1 g of sample due to lack of filter weights. In addition to the elements in Table I, Hg, As, and Zn were also observed.

These figures have to be taken only as an indication of the possible profile of an aerosol sample from a Buenos Aires residential neighbourhood. The results are only preliminary and are considered as semi-quantitative, due to several factors as the original sampling for other purpose than this study, the lack of control over the manipulations between the sampling stage and the analysis of the filters and the absence of a suitable standard.

As for XRF, due to difficulties with the instruments and without having an appropriate standard, only a qualitative assay was done for heavy and light elements, observing Fe, Mn, Zn, Pb, Cu, Ni, Ca and K.

Taking into account the characteristics of the results, no data evaluation was used on them. But they will serve to complete the aerosol characterization studies performed by the Air Pollution Centre of the Meteorological Service.

4. PLANS FOR FUTURE WORK

During 1993, sampling will be performed at designated sites of Buenos Aires. There is a possibility of sharing sampling sites with the Municipality as there is a project of re-activation of its sampling network, or at least part of it. Another offer has been to share their air filter samples for lead evaluation.

Irradiation experiences at the now available RA-1 are going to continue and although not immediately, there is a possibility of using this facility for short-lived nuclides analysis.

Emphasis will be put on standard preparation for both INAA and XRF and quality assurance.

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