

TRACE ELEMENTS AND ARTIFICIAL RADIONUCLIDES IN
BRAZILIAN ENVIRONMENTAL SAMPLES

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SUMMARY. Trace elements contents in aerosol samples as well as Cs-137 levels in fish and seawater were determined. The concentration of Al, Br, Ca, Ce, Cl, Cr, Fe, K, La, Mn, Na, P, Pb, S, Sb, Sc, Si, Sm, V and Zn were determined by ED-XRF and INAA. Data were analyzed by means of correlation coefficients, enrichment factors and absolute principal component analysis. Cs-137 levels in seawater varied from 0.5 to 2.2Bq.m⁻³ and for fish varied from 0.01 to 0.4Bq.kg⁻¹ of the edible part.

Key words: aerosol, air pollution, marine environment, cesium-137, artificial radionuclide, seawater, fish.

INTRODUCTION

In the last years there has been an increasing interest in various elements present in the environment and their possible effects on human health.

The pollutants can be transported across long distances from their emission source, removed from the atmosphere and deposited in the biosphere and hydrosphere by a number of mechanisms.

Artificial radionuclides, such as cesium-137 are produced regularly in nuclear power plants and can reach the environment by means of effluent discharges, nuclear weapons tests and from accidental releases as the Chernobyl accident. This radionuclide is important due to its nuclear and chemical characteristics. It has long physical half life, high fission yield and chemical behaviour similar to K. This radionuclide can enter to the human population by several

pathways and one of them is the marine environment.

Considering these problems and the lack of information concerning our country, it is relevant to investigate the trace element contents in aerosol samples as well as artificial radionuclide levels in marine samples.

EXPERIMENTAL

Aerosol Sampling

Aerosol samples were collected in the city of Sao Paulo, 1.5m above ground level, using a Dichotomous Sampler that fractionates suspended particles into two size fractions, 2.5 to 10 μ m (coarse particles) and less than 2.5 μ m (fine particles) on two 37mm teflon membrane filters with a flow rate of 1m³h⁻¹. In the total, 56 samples were collected. The collection time was 24h.

Seawater Sampling

The surface seawater was sampled at 8 fixed stations from the Brazilian coast from Rio Grande do Sul to Para States (from 52°02'S to 00°26'S latitude). Samples were acidified to pH 1 by adding concentrated hydrochloric acid and stored in 20L polyethylene containers.

Fish Sampling

Fish were purchased from fishermen's cooperative associations, who know the point of collection. Edible parts were used for the measurements. The main fish species analyzed were sardine, ballistes, weak fish, dog fish, mullet, saw fish, mackerel scad, brazilian croakar, red and white grunt.

Aerosol Analysis

The filters were previously analyzed by ED-XRF using a TEFA system which had a dual anode MO/W-X-Ray tube. The X-ray spectrometer consisted of a Si(Li) X-ray detector, amplifier and pulse height analyser.

After that, the filters were analyzed by neutron activation

analysis. Samples and standards were irradiated for 5 min under a neutron flux of about $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$, in order to analyse short-lived radionuclides. For the analysis of long lived radionuclides, samples were irradiated for 24h under a neutron flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$. Measurements were carried out after suitable cooling times with a Ge(Li) detector, Ortec model 8001-1022V, resolution of 2.6 keV at the 1332 keV gamma peak of ^{60}Co coupled to a 4096 multichannel gamma spectrometer, Ortec model 6240B.

Cs-137 Analysis in Seawater

Cesium-137 was preconcentrated from 100 liters of sample using ammonium phosphomolybdate (AMP), synthesized in our laboratory^{1,2}. Samples were counted in a high efficiency Ge detector, Ortec model 60210 over 1000 min. The efficiency curve was done employing standard samples from the IAEA.

Cs-137 Analysis in Fish

The edible parts (2kg) were weighed and dried at 110°C for one week and later on the temperature was gradually increased up to 450°C until ashes were obtained. Ashes were counted in a high purity Ge detector to determine Cs-137 levels.

RESULTS AND DISCUSSION

The elemental concentration data of aerosols were analysed by means of linear correlation coefficients, enrichment factor, principal factor analysis, PFA^{3,4}, and absolute principal component analysis, APCA⁵.

The results of correlation coefficients showed that Al, Ce, Fe, La, Sc, Si, Sm and Th have high correlation in the coarse fraction, while Br, P, S, Sb and V in the fine fraction. This seems to indicate a common origin of certain elements.

To evaluate the contribution of anthropogenic aerosol sources for each element, the enrichment factor was evaluated and the reference element utilized in this study was Fe. The results showed that Al, Ca, Ce, K, La, Mn, Rb, Sc, Sm are typical elements

of natural origin, while Br, Pb, S, V and Zn are representative of anthropogenic sources in the expected predominance of small particles.

Hereby, Fe concentration was used as a normalizing factor, assuming that all Fe was derived from the soil. This assumption is not strictly correct, once several activities may emit important quantities of Fe. Moreover many emissions have soil like composition. Thus, the enrichment factor represents at most the maximum enrichment in relation to the soil composition and should not be used as an indicator anthropogenic or natural sources of an element.

In order to identify pollution sources and to determine their relative contribution PFA and APCA were used. PFA gives the number of emission sources responsible for aerosol chemical composition, without a priori knowledge of these sources^{6,7}. For coarse particles, six factors explained 89% of the data variance. All elements presented high communality. The first factor was responsible for 31,8% of the variance and had high loadings for Al, Fe, Sc, Th, V and rare earths. It seems to represent the contribution from the resuspend soil. The second factor represented a high correlation with Ca, K, P, S and Si, whose presence was attributed to a fertilizer plant located 4km away from the sampling site. Only Cl and Na were separated in the third factor, which was clearly associated with marine aerosol. The fourth factor was associated with Br and Sb and it is probably owing to emissions from high temperature processes. Refuse incineration, a source known to be enriched in Zn, appeared to be represented in the fifth factor, it looks reasonable since had a municipal incinerator in operation near the sampling site during sample collection. The sixth factor had high loading for Cr and Pb and it was attributed to emissions from industrial processes. For fine particle matter, five factors were responsible for 83.2% of the total variance. In general, the interpretation of many of these factors was similar to that of the coarse particles. The influence of phosphatic rocks and refuse incineration appeared in the first factor.

APCA become possible the knowledge of the source, the source

profile and the relative contributions of each source to the atmospheric elemental concentrations. The relative contribution of each source was calculated as percentages of observed concentrations. For coarse particles the results showed that in the first component 94%Ce, 71%La, 69%Fe, 97%Sc, 60%Si, and 83%Sm were from resuspended soil. In the second component: 80%Ca, 50%K, and 49%P were from fertilizer plant. In the third component 22%Cl and 34%Na were associated with marine aerosol, with excess of Na. Finally, 80%Mn, 63%Zn, 46%Cr and 49%Pb were from refuse incineration and industrial processes, respectively.

Cesium-137 levels in Brazilian coastal seawater ranged from 0.5 to 2.2Bq.m⁻³. The error of the analysis was of 50%.

This radioactivity corresponds to typical fallout deposition values due to fallout for the southern hemisphere. Cesium-137 has been monitored by the European community member states and the Gesamp Report⁸ gathered data relative to the levels of this radionuclide in seawater and fish over the period from 1980 to 1985. The cesium-137 levels in Portuguese waters are low (<20Bqm⁻³) and include a significant contribution due to the fallout from nuclear weapons testes. Areas like northwest coast of Scotland and northern Ireland are influenced by input from Sellafield (cesium-137 levels 10-200Bqm⁻³) and the Irish Sea contains the highest concentrations determined (>200Bqm⁻³).

Cesium-137 concentrations in Brazilian fish varied from 0.01 to 0.4Bqkg⁻¹ while the values for European countries ranged from about 0.3 to 3.0Bqkg⁻¹ (wet) with the higher levels being found in the Baltic Sea. Bettencourt et al⁹ determined cesium-137 contents in fish in the range from 0.1 to 1.7Bqkg⁻¹ in muscle of collected in Portuguese oceanic waters. From the artificial radionuclides analysed, Cs-137 is the most significant contributor for the dose to man through fish consumption.

In this work, cesium-137 levels obtained for marine samples are in agreement to the published values in the literature and they can be considered reference levels to Brazil. Any increase in these levels could be attributed to some possible future contamination.

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