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Scanning proton microprobe applied to analysis of individual aerosol particles from Amazon Basin

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Abstract

The development of the Scanning Proton Microprobe (SPM) offers a new possibility for individual aerosol particle studies. The SPM joins Particle Induced X-ray Emission (PIXE) elemental analysis qualities with micrometric spatial resolution. In this work the Lund University SPM facility was used for elemental characterization of individual aerosol particles emitted to the atmosphere in the Brazilian Amazon Basin, during gold mining activities by the so-called "gold shops".

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1. Introduction

In recent years gold mining and gold prospecting areas in Brazil have become an important environmental issue. Gold mining creates a great diversity of problems of economic, political, social and environmental nature. In the past decade gold mining activities in Amazon have been responsible for a release of around 100 tons of mercury per year. Metallic mercury in gold mining activities is used to amalgamate particulate gold. During this process losses of Hg to soil, rivers and the atmosphere occur. For the production of each kilogram of gold, between 1 and 2 kg of Hg are released into the environment.

Mercury has no known metabolic function in human beings. Therefore, even low concentrations in the body may be regarded as a potentially harmful. The human toxicity of mercury depends on the Hg chemical forms in which it occurs and on the level of exposure to different mercury sources (air, water and food) and through different routes (inhalation, ingestion and dermal contact).

Large Hg emissions affecting the atmosphere in the Amazon Basin occur through amalgam burning [1–3]. In the atmosphere more than 95% of Hg occurs in its volatile gaseous form, Hg^0 [4–6]. The remaining non-elemental form is associated with aerosol particles. Mercury emissions in the

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Amazon Basin occur in rural and urban areas. Gold mining generally is done far from urban areas and the first burning of amalgam almost always takes place near the gold mining area. A second amalgam burning occurs in general at gold shops in urban sites. The percentage of Hg in the amalgam brought into the gold shops varies between 2% and 10% of the gold mass.

The municipality of Alta Floresta, located in the north of the Mato Grosso state, in the Amazon Basin, was founded in 1979. Its climate is typical of the Amazon Basin, hot, humid and tropical, with temperatures ranging from 23°C to 37°C, with heavy rainfall during the wet season. The gold rush of the 1980s replaced rural development by gold mining activities. The gold production is much higher in the dry season (June–September) because heavy rain makes it difficult to work along the rivers. So, the peak of gold mining activities coincides with the biomass burning period in the region, responsible for a release of large amount of fine particles ($d_p < 2$ μm) into the atmosphere [7]. The urban area of Alta Floresta contains several gold-dealing shops, where about 25 tons of gold are purified and commercialized annually. Between 0.5 and 2.5 tons of Hg are emitted annually in the urban area of Alta Floresta [8].

The objective of this work is to characterize the particulate matter emitted to the atmosphere during the gold purification by the Alta Floresta gold shops. The elemental characterization of individual particles released during the amalgam burning process in the gold shops was performed. The association between Hg and other important aerosol sources such as soil dust and biomass burning aerosol particles [7] was also studied.

2. Experimental methods

Characterization of the Alta Floresta atmospheric aerosol was carried out during two field campaigns. They took place in August and September 1992 and 1993, both during the peak of the biomass burning season. Fine and coarse mode aerosol particles were collected using stacked filter units (SFU). The SFU were fitted with an inlet, with 50% aerodynamic cutoff diameter of 10 μm. The SFU collects coarse mode particles ($2.0 < d_p < 10$ μm) on a 4.7-mm-diameter, 8 μm pore-size Nuclepore filter, while a 0.4 μm pore-size Nuclepore filter collects the fine mode particles ($d_p < 2$ μm) [9]. The flow rate in the SFU was typically 14 l/min which results in a 50% cutoff diameter at 2 μm between fine and coarse fractions of the aerosol. During this field campaign several samples were collected in Alta Floresta environment and in the Alta Floresta gold shops, both indoor and in the exhausts of the gold shops' chimneys. Elemental concentrations were measured by Particle Induced X-ray Emission (PIXE) [10]. The results of the PIXE bulk analyses of these samples can be found in Refs. [4,7,8].

In this work we present the analyses of several individual particle elemental compositions. These particles were collected directly in the gold shops' chimney exhausts. They were collected in two filters sampled in the field campaigns: one corresponding to the fine mode and the other to the coarse mode. Their elemental composition were measured by Scanning Proton Microprobe (SPM) [11].

In SPM analysis, a well-focused beam of high energy protons is scanned over the sample. One of the major advantages of this technique is the excellent detection limit, of the order of 2–20 ppm, depending on the SPM design, experimental conditions and detection geometry. In this work a 2.5 MeV focused proton beam (2.5 μm diameter) generated by the single-ended NEC-3UH accelerator from Lund University SPM was used [12]. The aerosol samples were mounted in an evacuated target chamber which holds up to twelve samples simultaneously. To facilitate the visual inspection and locating of interesting parts of the samples a microscope with micrometer scale is inserted into the target chamber. The proton beam is scanned over the sample using a magnetic lens system [13]. The scanning is controlled by a versatile computer system which facilitates a flexible software controlled scanning [14].

Proton-induced X-ray events are acquired by means of a Si(Li) detector system and stored in list mode (event-by-event) for off-line analysis. An on-line sorting [15] allows a real time X-ray intensity image recording of elemental maps of the sample.

The off-line sorting process also includes the elemental analysis of pre-defined regions of the sample, using the construction of masks. These masks allow the independent elemental quantification of various individual particles present in the same sample scan.

More than 130 individual particles were analyzed from fine and coarse mode aerosol. Data interpretation was done applying multivariate statistical analysis. We have used the multivariate IDAS package [16] for our data reduction and interpretation.

3. Results and discussion

Seventy seven individual aerosol particles from the coarse fraction of the aerosol emitted from the gold shop chimneys were analyzed. Applying IDAS hierarchical cluster analysis program and using the Euclidean distance method, four main clusters were identified. The number of clusters was defined using Sum of Distances (SD) [16] and Davies–Bouldin index (DB) [17] criteria, shown in Fig. 1. SD criterion is based on the statistical idea that the "best" clustering should lead to formation of compact clusters, i.e. total within-cluster variation (error sum of distance squares) should be minimal. The minimum of this criterion indicates the formation of the most compact cluster structure. DB is based on the measure of within-to-between cluster spread. The smaller the criterion the better clustering is achieved. Under favorable conditions the minimum of the criterion corresponds to the most compact (minimum of error sum of squares) and at the same time the most separated (maximum of the distance between the centers of the clusters) clusters. The comparison of this criterion with DB shows that their minima may not coincide. If they however, coincide, it means that the most compact clusters are at the same time the most separated ones.

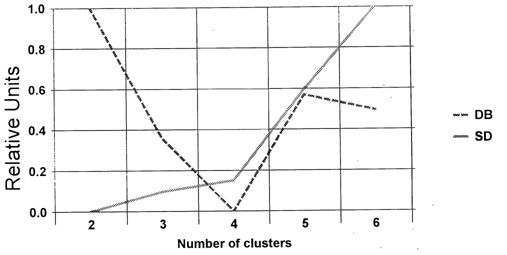

Fig. 1. Sum of Distances (SD) and Davies–Bouldin index (DB) criteria for cluster analysis of coarse mode individual particle elemental concentrations.

The average elemental concentrations associated with each of the four clusters selected are shown in Fig. 2. Cluster 1 accounts for majority of the analyzed particles (49 particles). This cluster is related with high concentrations of P, Pb, Hg, Au, Fe, S and K, showing an association of amalgam burning emission (Hg and Au) with particles from biomass burning and natural biogenic aerosol, enriched in S, K and P. The second and the third cluster are very similar, responsible for 25% of the particles (11 and 8 particles, respectively). Again high concentrations of Au and Hg are present in these clusters, but the presence of great amounts of Si and Fe indicates an association between soil dust and amalgam burning emission. The fourth cluster, with nine particles, has large amounts of P, with almost no Hg and Au. This cluster represents the natural biogenic contribution to the aerosol. Pb is present in all of the clusters and is a probably contaminant from the chimney.

The analysis of individual particles from the coarse mode aerosol demonstrates a strong association of Hg with the three most important aerosol sources in the Alta Floresta region: biomass burning aerosol; biogenic aerosol and soil dust. Fig. 3 shows the number of elemental concentration above the SPM detection limit (non-zero occurrences) for the particles associated with the clusters. It is possible to see that SPM was able to measure several elements for the majority of the identified individual particles.

The beam size of the Lund SPM (2.5 μm diameter) was too large to analyze individual particles in the fine fraction of the aerosol. However, the SPM allows us to identify several clusters of particles present in the fine mode aerosol. So, 62 independent aerosol particle agglomerates were irradiated and analyzed in the same way as the coarse mode individual particles. Using the SD criterion and DB criterion (Fig. 4), four clusters were

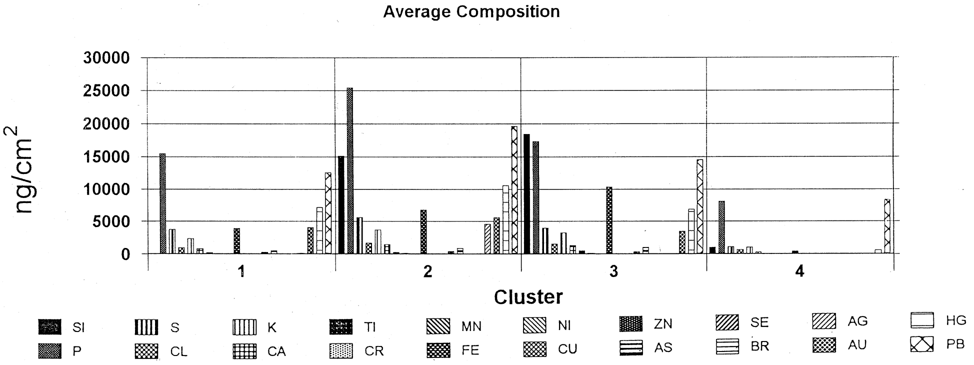

Fig. 2. Average elemental concentrations associated with each of the four clusters for the coarse mode aerosol.

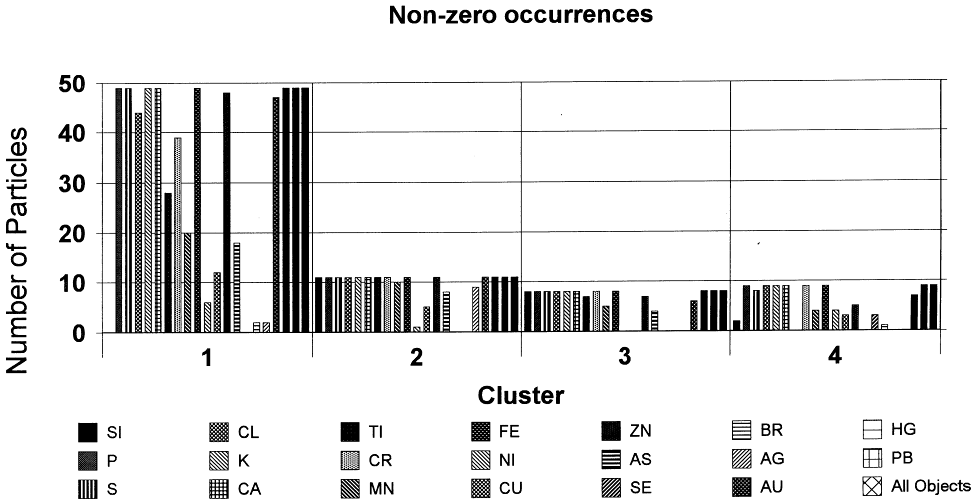

Fig. 3. Concentrations above the elemental detection limits for the particles associated with all the clusters in the coarse aerosol fraction.

defined. The average elemental composition of the fine mode agglomerates associated with each of the four identified clusters are shown in Fig. 5. The first cluster contains the majority of the agglomerates (49 agglomerates). This cluster is defined basically by high concentration of P, Pb and Fe, with also some contribution of K, S and Cl. The second cluster is responsible by 11% of the fine particles' agglomerates and is well characterized as soil dust, with a large amount of Si, P, Fe and Pb. Five agglomerates are associated with the third cluster, characterized by P and Fe. Only one agglomerate, very rich in Ti, defines the fourth cluster.

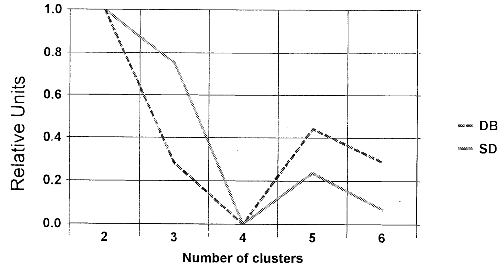

Fig. 4. SD and DB criteria for cluster analysis of fine model particle agglomerate elemental concentration.

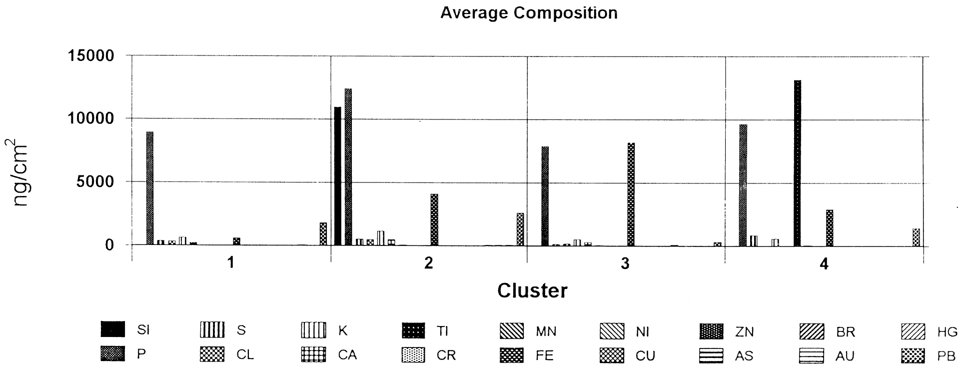

Fig. 5. Average elemental concentrations associated with each of the four clusters for the fine mode aerosol.

The identification of a relation between gold shop emissions and the other major aerosol sources in Alta Floresta is not so clear for the fine fraction of the aerosol as it is for the analysis of the coarse fraction. The main reason for this difficulty is an insufficient spatial resolution of the SPM to analyze the fine mode aerosol. Detection limit was also a limiting factor during this analysis. In the SPM analysis Au concentration was above its detection limit in only five fine particles' agglomerates, and Hg concentration could be measured in only three agglomerates.

A comparison between the SPM results with PIXE bulk particle analysis shows the utility of coarse mode SPM individual particle analysis. Principal Factor Analysis (PFA) [18] of the bulk PIXE elemental concentrations determined for all samples collected at the gold shops' chimneys show three components for the coarse mode aerosol [4]. The first component is associated with soil dust, relating Si, Ca, Ti, Fe, Cu and Au. The second component associates Hg, Pb and Au to a biomass burning aerosol component, while the third component, with P, S, K, Au, Hg and Pb, was identified as a gold shop emission, associated with the natural biogenic aerosol release. The PFA could not detect the association between Hg and soil dust, verified by the SPM individual particle analysis.

Bulk analysis of the fine aerosol emitted by the gold shops [4] also could not determine a clear relation between Hg and the major aerosol sources in the region. On the other hand PFA of the fine mode bulk PIXE analyses was able to identify a clear contribution of the amalgam burning to the fine mode aerosol. This contribution has also a significant correlation with S, P and Cl concentrations.

4. Conclusions

In this work the utility of a Scanning Proton Microprobe technique in the analysis of the coarse mode aerosol was demonstrated. A strong association was verified among Au–Hg amalgam burning aerosol and the other three important aerosol sources in the Amazon Region: biogenic aerosol; soil dust and biomass burning aerosol. This association creates a new mercury transport mechanism in the environment. This transportation mechanism can assume an important role in the Hg dispersion since the peak of gold mining activities coincides with the biomass burning season, when the inhalable aerosol concentration jumps from a background concentration of 25 $\mu g/m^3$ to values greater than 150 $\mu g/m^3$ [4,7,8]. The results obtained for the fine mode aerosol are not clear because the lateral resolution of the Lund's SPM was not sufficient to perform individual particle analysis of submicrometer particles. A comparison between SPM and bulk PIXE analysis shows an agreement between these two sets of results. It also demonstrates their complementary characteristics.

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