Large scale mercury and trace element measurements in the Amazon basin

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Abstract

Large emissions of mercury (Hg) occur in the Amazon Basin as a result of gold mining activities. Mercury and aerosol particles were collected in the Amazon basin, as part of the SCAR-B – Smoke Clouds and Radiation – Brazil experiment in August and September 1995. Three airplanes were used to collect total mercury and aerosol particles. Sampling was performed with the University of Washington Lockheed C131A airplane, as well as in two Brazilian Bandeirante EMB 120 planes. Atmospheric mercury was sampled using two gold traps in series for each sampling line and measured with atomic fluorescence spectrometer (AFS). Aerosols were collected on Teflon and polycarbonate filters and analyzed by particle-induced X-ray emission (PIXE) for up to 20 elements, and by instrumental neutron activation analysis (INAA) for up to 39 elements. Absorbing aerosols expressed as black carbon (BC), and aerosol gravimetric mass were also determined. Sampling time was 2–4 h. The sampling period was at the peak of the biomass burning season, when most of the Hg is emitted. Concentrations for total Hg in this study were as high as 14.8 ng m^{-3}. Factor analysis was performed for the combined (aerosol and Hg) data set and six factors were observed: A soil dust component; a biomass-burning factor (with fine mode mass concentration, BC, K, Cl, Zn and others); a natural biogenic component (P, K, S, Ca, Mn, Zn); a second soil dust factor (enriched in Si); a sea-salt aerosol component, with NaCl; and a factor related to gold mining activities, with Hg, Pb and other elements. Hg was also clearly associated with the biomass-burning component, in addition to the gold mining activities component. An average of 63% of the Hg concentrations was associated with the gold mining activities. About 31% of the Hg concentration was associated with the biomass-burning component, the soil dust accounted for 4% and the NaCl component for 2.1% of the airborne Hg concentrations. The high association between Hg and biomass burning can be caused by at least three mechanisms: (1) adsorption of gaseous Hg on existing biomass burning particles; (2) direct release of Hg from the vegetation to the atmosphere during forest burning; (3) evaporation of Hg from soil during the forest burning. Three-dimensional long-range air mass trajectory analyses show the possibility that Hg exits the Amazon Basin over two main routes: to the South Atlantic, and to the Tropical Pacific, over the Andes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Amazonia; Mercury; Aerosol particles; Aircraft sampling; Heavy metals

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1. Introduction

Mercury release from gold mining activities and deforestation are the two most important environmental

issues in the Amazon Basin. Gold mining activities in Amazonia have been responsible for the release of about 2000–3000 t of Hg over the last 20 y. Annually about 200 t of Hg is released in the Amazon basin and 65–83% of this amount is released to the atmosphere (Hacon et al., 1995; Lacerda and Salomons, 1991). Metallic Hg is used to amalgamate gold and during this process, losses of Hg to the environment occur at two distinct stages. Through manipulation of metallic Hg in the separation of gold from gravel, Hg is lost to rivers and soils. Large emissions to the atmosphere occur through amalgam burning. For the production of each kg of gold between 1 and 2 kg of Hg are emitted into the environment (Pfeiffer and Lacerda, 1988; Pfeiffer et al., 1989). Gold production has been decreasing sharply in Amazonia since 1989 (Lacerda, 1997; Barbosa et al., 1995). It is estimated that in 1989, about 2000 mining sites provided jobs for nearly one million prospectors, being the major source of income in the region. High Hg concentrations observed in fish and in the hair of the indigenous people living very far from the mining areas, and even in pristine Northern Amazon basin, stay unexplained, but regional atmospheric transport could be responsible for part of this high mercury concentration (Barbosa et al., 1995; Barbosa, 1997). Contamination in lakes was strongly associated with human exposure and gold mining activities in the Amapá region in Amazonia (Guimarães et al., 1999). Some parts of Amazonia have soils rich in Hg, as reported by Roulet et al. (1998), with concentrations of 90–210 ng g^{-1} dry weight.

Mercury is present in the atmosphere in the forms of Hg^0, Hg(II), and some other minor components (such as methylmercury species) in gaseous and particulate phase, Hg$_{(p)}$ (Schroeder and Munthe, 1998; Fitzgerald et al., 1998; Bergan et al., 1999). The residence time of Hg^0 in the atmosphere is long, with current estimates ranging on the order of 0.5–2 yr (Lindqvist and Rodhe, 1985; Schroeder and Munthe, 1998; Fitzgerald et al., 1998). The aerosol component has a resident time of the order of days, or at most, a few weeks. Very few studies have been performed on interactions between terrestrial vegetation and the biogeochemical cycling of Hg (Lindberg et al., 1991).

Biomass burning in tropical forests also seems to have contributed significantly to the Hg release to the atmosphere. Veiga et al. (1994) discussing Hg emissions through biomass burning in the Amazon basin estimates a large emission of Hg to the atmosphere, at levels of about 90 t annually. They considered 0.05 ppm as the natural level of Hg in the vegetation with an average Hg release efficiency by biomass burning of 90% for above ground biota. There are several mechanisms responsible for the Hg release through biomass burning. Naturally the forest contains Hg that is volatilized during combustion of the forest. Hg from soils is also emitted in the fires, due to the high temperature near the ground, and the

strong vertical convective movement. Mercury, that has already accumulated on the forest and soils historically, especially during the last 20 yr, will be re-emitted to the atmosphere during forest burning. The Amazon Basin contains the world's largest rain forest, covering an area of about 4×10^6 km^2. This region has intense convective activity, resulting in rapid vertical mixing of gases and aerosols to high altitudes where they are transported over long distances with a consequent impact on the global tropospheric chemistry (Artaxo et al., 1988, 1990). The biomass burning period extends from July to the end of September and coincides with the peak period of gold mining activities, with high Hg emissions. The aerosol particle loading increases from a natural background value of 10–20 μg m^{-3} to values as high as 700 μg m^{-3} over large areas in Amazonia, even far from the biomass burning regions. Large amounts of fine mode aerosol particles ($d_p < 2$ μm) are released into the atmosphere, altering its chemical composition (Artaxo et al., 1988, 1994). These particles play an important role in the transport of particulate Hg or aerosols with adsorbed gaseous Hg in the surface over long distances, since particles between 0.1 and 1 μm have relatively long atmospheric residence time. (Crutzen and Andreae, 1990; Andreae et al., 1998). In 1995, during this experiment, the Brazilian space agency estimated 29,059 km^2 as the area deforested in the Amazon basin, being the largest deforestation area in Amazonia from 1990 to 1999.

In a natural tropical forest atmosphere, vegetation plays a major role in controlling the biogenically produced airborne particle concentration. The forest vegetation is the main natural source of atmospheric organic particles globally (Artaxo et al., 1988, 1990). The natural biogenic aerosol particles consist of many different types of particles, including pollen, spores, bacteria, algae, protozoa, fungi, fragments of leaves and other types of particles (Artaxo et al., 1994). These natural biogenic particles can be sub-micrometer in size (Artaxo and Hansson, 1995). Recently the possibility of mercury emission by the vegetation was established for different forests in the Northern Hemisphere (Lindberg et al., 1998), but the issue of Hg emission for tropical forests is still open.

The objective of this work is to make a large-scale characterization of atmospheric Hg concentration in the Amazon basin. Aircraft sampling of Hg and aerosol particles can provide tools to study the association between biomass burning and airborne Hg concentrations and to measure Hg atmospheric concentrations over large areas. Using multivariate statistical analysis, the relationships between total Hg and the aerosol sources in the dry season in the Amazon Basin are being studied. The results obtained shows that biomass burning aerosol particles are related to atmospheric Hg in the Amazon basin. A complete characterization of biomass burning aerosol and long-range atmospheric transport in the Amazon basin were studied in other reports from the

SCAR-B experiment. (Artaxo et al., 1998; Trosnikov and Nobre, 1998; Nobre et al., 1998; Feitas et al., 1997).

2. Sampling and analytical methodologies

Total mercury and aerosol particles were sampled during the SCAR-B experiment in August and September 1995 (Kaufman et al., 1998). The SCAR-B experiment was coordinated by NASA, University of Washington, INPE (Brazilian Instituto Nacional de Pesquisas Espaciais), and the University of São Paulo. The main objective of the SCAR-B experiment was to study the radiative properties of aerosol particles emitted by biomass burning in Amazonia. The experiment consisted of airborne campaigns that covered most of the area of the Amazon Basin and cerrado regions. Three airplanes were used to collect total mercury and aerosol particles. The University of Washington Lockheed C131A airplane is fully equipped to collect aerosols and trace gases, as well as to measure radiative properties of aerosol particles. Two Brazilian Bandeirante EMB 120 planes, specially instrumented to collect Hg and aerosol particles were also used (Artaxo et al., 1998; Kaufman et al., 1998).

In this investigation, airborne mercury was collected in gold traps that consist of a mixture of small pieces of solid gold and quartz glass in an approximate ratio of 1 : 1, contained in sampling tubes of quartz with a length of 12 cm, with an internal diameter of 0.4 cm. Newly prepared gold traps were soaked in concentrated HNO_3 overnight and rinsed thoroughly in distilled and Milli-Q water. The traps were then heated for several minutes to $600°C$ while purified N_2 gas flowed through them. Once the blank values were checked, the traps were sealed with Parafilm and stored in clean plastic bags. Quartz traps of the same dimensions were used, which was intended to collect particulate mercury from the air. The sampling setup for Hg has been described previously (Xiao et al., 1991). A quartz trap was placed ahead of two gold traps in series for each sampling line. The sampling volumes were registered with precision mass flowmeters, and the sampling flow rate was $1\,l\,min^{-1}$ for a time interval from 2–4 h. After sampling, the exposed gold traps were carefully sealed in pre-cleaned plastic bags and stored in a freezer. Using a two-stage gold trap analysis technique, the Hg collected in the individual sampling trap was desorbed by heating and transferred to an analytical trap with purified helium as carrier gas. The analytical trap was then heated and the Hg thus released was analyzed by atomic fluorescence spectrometer (AFS). The detection limit was about 0.2 pg Hg, which corresponds to a detection limit of $0.002\,ng\,m^{-3}$ for an air sample of $0.1\,m^3$, the minimum volume under this experiment. Field blanks were transported and analyzed in an identical procedure to that used for real Hg samples.

Aerosol particles were collected using $0.4\,\mu m$ pore size, 25 mm diameter Nuclepore polycarbonate filters and 47 mm diameter, $1\,\mu m$ pore size Teflon filters. Samples for total Hg were collected in parallel to the aerosol samples. The inlets used were isokinetic with a flow rate of 10 lpm in m^{-1} (liters per minute) for the Nuclepore filters and 25 lpm in m^{-1} for the Teflon filters. The cut-off aerodynamic diameter was about $6\,\mu m$. Aerosol blank filters were taken at each of the 5 collected filters, subjected to the same analytical procedures.

Elemental concentrations for the Nuclepore filters were measured by particle-induced X-ray emission (PIXE) (Johansson et al., 1995). Concentrations for 19 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Zr, and Pb) were determined. A tandem nuclear accelerator "Laboratório de Análise de Materiais por Feixes Iônicos" (LAMFI) was used for the PIXE analysis at the University of São Paulo. Detection limits were typically $5\,ng^{-3}$ for elements in the range $13 < 22$ and $0.1\,ng\,m^{-3}$ for elements with $Z > 23$ (Artaxo and Orsini, 1987). The aerosol mass concentration was obtained through gravimetric analysis of the filters. Black carbon concentration was measured by a reflectance technique using a photometer. Elemental concentrations for the Teflon filters were determined by instrumental neutron activation analysis (INAA) at the University of Gent. The INAA involved two separate irradiations (one for 5 min and one of 7 h) in a thermal neutron flux of 2–$3 \times 10^{12}\,n\,cm^{-2}\,s^{-1}$ in the Thetis reactor of the University of Gent. Up to 39 elements were measured by INAA, i.e., Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Lu, W, Au and Th. Details of the INAA experimental procedure can be found in Schutyser et al. (1978).

To analyze the relationships between the several measured variables, absolute principal factor analysis (APFA) was used (Thurston and Spengler, 1985). APFA offers the possibility to obtain a quantitative elemental source profile instead of only a qualitative factor-loading matrix as in traditional applications of factor analysis. A model of the variability of the trace element concentrations is constructed so that the set of intercorrelated variables is transformed into a set of independent, uncorrelated variables. In the APFA procedure one obtains the elemental concentration contribution of each identified component after calculating the absolute principal factor scores (APFS) for each sample (Artaxo et al., 1988, 1990). The elemental concentrations are subsequently regressed on the APFS to obtain a quantitative contribution of each element for each factor. The measured total Hg concentrations can also be regressed on the APFS to obtain the quantitative relationship between the measured Hg concentrations and the retained factors. These regressions were performed with no additive term, so the model tries to explain all the observed concentration
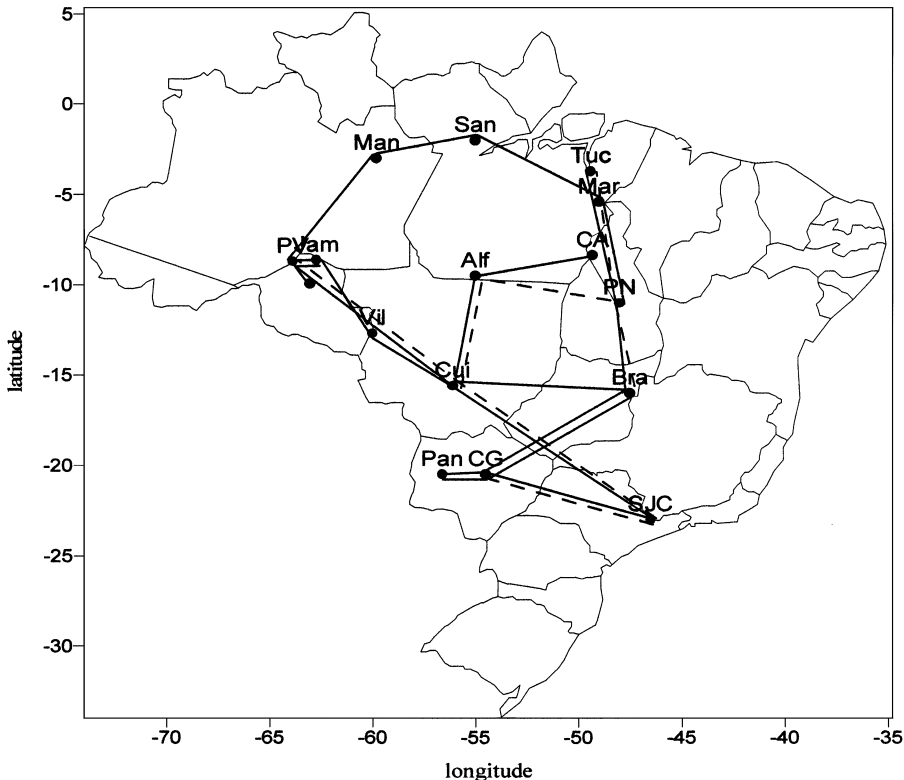
SCAR-B - 1995

Fig. 1. Location of the flights by the three airplanes. Most of the Amazon basin and part of the Brazilian cerrado region was covered in the airborne measurements. The cities and areas where the flights took place are: CG: Campo Grande, SJC: São José dos Campos, PN: Porto Nacional, Bra: Brasília, Cui: Cuiabá, Alf: Alta Floresta, Pan: Pantanal, Jam: Jamarí, PV: Porto Velho, Tuc: Tucuruí, Vil: Vilhena, Man: Manaus, San: Santarem, Mar: Marabá.

with the retained factors. The software package SPSS for windows version 9 was used in statistical calculations.

The airborne campaign was made from 1 August to 15 September 1995, using three airplanes, and the flight tracks covered most of the area of the Amazon basin (Kaufman et al., 1998). Fig. 1 shows the location of the flights. The three main gold mining areas in the Amazon basin are located in Rondônia state (near the cities of Porto Velho, code PV, Jamarí, Jam, and Vilhena, Vil), near the city of Alta Floresta (Alf), and in the South of the Pará state (near the city of Marabá, code Mar). It is important to emphasize that the measured Hg concentrations do not reflect only local concentrations and emissions. The intense convection in the Amazon basin, the flat terrain and meteorological conditions (Nobre et al., 1998) make regional Hg transport quite efficient. The general circulation pattern is from the Pará state, following the Amazon, Rondônia, Mato Grosso states and the plume leaves South America in the Southern part of Brazil (Trosnikov and Nobre, 1998). The samples were collected in many geographically and meteorologically

different conditions. Some were collected over areas with intense biomass burning, other over areas with very little smoke, with predominance of natural biogenic emissions. Still other samples were collected near areas with strong Hg emissions (Alta Floresta and Rondônia, for example). Flight altitudes also varied, with samples collected between 1000 and 5000 m altitude. It is also important to note that the samples represent average Hg concentration for 2–4 h collection time. Over some urban areas in the Amazon basin such as Alta Floresta, ground-based Hg concentrations were measured at more than 1000 ng m^{-3} (Hacon et al., 1995). A full description of the meteorological conditions prevailed during the experiment can be obtained from the work of Nobre et al. (1998).

3. Results and discussions

The Hg sampling system used in this study consists of two quartz tubes, the first with only quartz, designed to

collect the particulate Hg (that typically is about 5% of total Hg (Lindqvist, 1991; Xiao et al., 1991), and the second quartz tube with gold and quartz wool, that collects the gaseous Hg. In this investigation, however, it was noticed that a large portion of Hg was collected in the quartz traps for most of the sampling lines. Especially for samples collected over heavy biomass burning impact, the quartz wool changed color from white to gray or black. In some extreme cases, the Hg found from some of the quartz traps was even higher than in that from the gold traps. It is not possible to know if the detected Hg in the quartz traps reflects the real particulate Hg concentration in the air generated by biomass-burning activities, or the detected Hg was formed secondarily through adsorbing elemental Hg on black carbon, which was already collected in the quartz trap. A careful laboratory test was performed at the University of Gothenburg using quartz traps loaded with little carbon to give similar color as those exposed traps. Elemental Hg was then delivered into the traps as a carry gas flow rate of $1 \, \text{lpm}^{-1}$. Result showed that almost 50% of the Hg^0 were collected by the grey colored quartz trap, which makes it impossible to distinguish which portion is primary particulate Hg in the air and which part is sampling artifact. Therefore, only total mercury, all those found in both the quartz and gold traps is reported in this paper. The difficulty in separating the different Hg components was discussed in detail in the intercomparison work of Ebinghaus et al. (1999).

A total of 64 Hg samples were collected in this experiment, following the flight tracks showed in Fig. 1. The samples were collected over many different areas and altitudes, and represents averages of 2–4 h sampling time. The average Hg concentration was $3.05 \, \text{ng m}^{-3}$, with a maximum of $14.8 \, \text{ng m}^{-3}$ for the region of Rondônia, dominated by gold mining activities. This value is a little higher than the reported Hg concentration in the background ambient air. For example, $2.25 \, \text{ng m}^{-3}$ was observed over Northern Atlantic, and $1.50 \, \text{ng m}^{-3}$ over Southern Atlantic (Slemr and Langer, 1992). A reference value of $2.9 \, \text{ng m}^{-3}$ was obtained by Iverfeldt et al. (1995) over Southwest Sweden. Values of total gaseous Hg of $1–2 \, \text{ng m}^{-3}$ were observed in the Arctic (Schroeder et al., 1998). Over forested areas, Xiao et al. (1991) report Hg concentrations of $2.1 \, \text{ng m}^{-3}$ for South Sweden in a coniferous forest, and Lindberg et al. (1992) report $5.8 \, \text{ng m}^{-3}$ for a deciduous forest in Tennessee. In a background site in Southern Germany, Hg concentrations was observed in the range of $2–3 \, \text{ng m}^{-3}$ (Slemr and Scheel, 1998). It should be emphasized that the intense convection in the Amazon basin together with the flat terrain makes regional Hg transport quite efficient. Fig. 2 shows a plot of the measured Hg concentrations. High concentrations were observed in Rondônia and Alta Floresta, areas where strong gold mining exists (Hacon et al., 1995; Pfeiffer et al., 1989). Ground based total Hg measurements in the urban area of Alta Floresta showed concentrations up to $1000 \, \text{ng m}^{-3}$ (Hacon et al., 1995). In these areas, a strong biomass-burning aerosol component was also observed. Very low Hg concentrations ($0.5–2 \, \text{ng m}^{-3}$) were observed over pristine primary forest areas. Meteorological factors such as the frequent rains and strong cloudiness may influence the airborne Hg concentrations. The flights on this experiment were made over changing relative humidity (from 25 to 90% RH) and temperatures (25 to 35°C) in this study, any relationship of Hg concentrations with altitude or meteorological parameters was not observed.
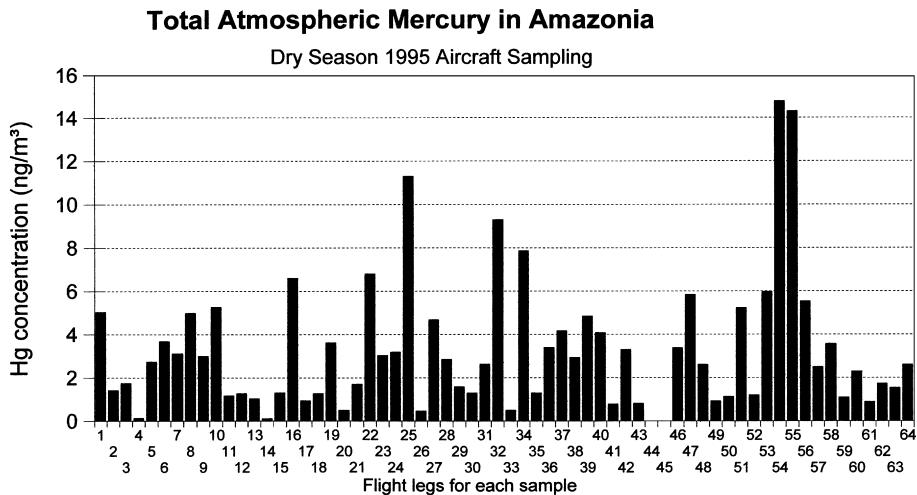

Fig. 2. Total atmospheric Hg concentrations measured for each flight leg in the Amazon basin.

Table 1

Average, standard deviation, minimum and maximum concentrations in ng m^{-3} for all species measured. The trace elements, black carbon and mass are for the aerosol phase and Hg (total) represents the gaseous and particulate Hg

Element	Average (ng m^{-3})	SD (ng m^{-3})	Minimum (ng m^{-3})	Maximum (ng m^{-3})	N[b]
Na	95.4	59.2	30.0	270	43
Mg	659	381	196	2356	43
Al	2291	1787	350	7297	43
Si	3126	2080	713	8673	43
P	140	135	3.50	559	43
S	1198	889	59.0	4333	43
Cl	233	247	27.6	1291	43
K	1581	1064	137	5581	43
Ca	1297	1220	36.2	5723	43
Sc	0.37	0.35	0.041	1.47	43
Ti	121	122	9.29	533	43
V	4.03	3.86	0.54	17.6	43
Mn	71.8	86.7	10.9	471	43
Fe	1132	974	76.9	4328	43
Cu	2.91	1.69	0.64	8.78	43
Zn	10.9	6.53	1.92	27.7	43
Ga	0.51	0.36	0.006	1.46	43
Br	12.8	8.19	2.40	36.9	43
Rb	8.83	5.26	1.55	25.9	43
Sr	17.3	15.9	1.44	67.1	43
I	3.83	2.09	0.65	9.19	43
La	0.79	0.61	0.19	2.97	43
Sm	0.12	0.094	0.003	0.42	43
Pb	7.19	4.59	2.05	17.9	17
Th	0.36	0.23	0.05	1.17	43
Hg (total)	3.05	2.49	0.10	14.8	43
BC[a]	5.49	3.87	0.23	17.5	43
Mass[a]	105	61.8	8.21	297	43

[a] Mass is the gravimetric aerosol mass concentration in μg m^{-3}. BC is the black carbon concentration in μg m^{-3}.

[b] N is the number of samples where the element was measured above the analytical detection limits.

Table 1 shows the average, minimum and maximum concentrations in ng m^{-3} for the species measured. The aerosol mass concentration has an average value of 105 μg m^{-3}, with a maximum of 297 μg m^{-3}. These values are of very high aerosol concentrations. Black carbon (BC) averages 5.49 μg m^{-3} comprise 5–15% of the aerosol load in mass. This high BC concentration, which originates from biomass burning, is associated with small particles (Martins et al., 1998) and represents a large surface area for the adsorption of gaseous Hg. Consequently, Hg could be associated with the biomass burning component, but it could not necessarily be emitted simultaneously with the pyrogenic particles. Sulfur and trace elements associated with anthropogenic activities (like V, Cu, Zn and others) are present in low concentrations. INAA has excellent detection limits for gold (down to 2 pg m^{-3} for the air volumes sampled), but blank variability did not allow the measurement of gold in most of the aerosol samples.

Fig. 3 shows the aerosol mass concentrations for the individual samples. Very high aerosol concentrations are generally observed. The sample with concentration near 300 μg m^{-3} was collected in Alta Floresta, an important gold mining center in Amazonia, and also an area with intense regional biomass burning. It can also be observed from Fig. 3 that there is a background aerosol mass concentration of about 10–20 μg m^{-3}, which was observed in samples not directly impacted by biomass burning emissions. The high concentrations of aerosols were also observed in the visible channel of the GOES-8 satellite. This indicated the presence of plumes extending over more than 8 millions km^2 in South America (Prins et al., 1998). Fig. 4 shows the black carbon concentration for each aerosol sample. Black carbon is a good tracer for biomass burning emissions. High levels of BC were observed over Alta Floresta and Rondônia areas, where intense biomass burning occurs every year during the dry season (Artaxo et al., 1998; Echalar et al., 1998).

The factor analysis results are expressed in terms of the factor-loading matrix that express the relationship between each original variable and the retained factors. Table 2 shows the factor-loading matrix for the 6 components observed in the data set. In addition, factor analysis solutions with 4 and 5 factors were studied, but the 6-factor solution was the best from several statistical point of view. The factor analysis calculations were performed on a sub set of 43 samples, because Teflon filters were not available for the last part of the experiment. The number of samples is not ideal for factor analysis calculations, but the data set was checked by several statistical tests provided by the software package SPSS for windows. Three tests were performed on the data set: (1) Kaiser–Meyer–Olkin test that measure the sampling adequacy, calculating the partial correlations among variables, (2) Bartlett's test of Sphericity tests whether the correlation matrix is an identity matrix, which would indicate that the factor model is inappropriate, (3) calculation of the anti-image correlation matrix. The data set has passed all these three statistical criteria. The commonalities in the last column of Table 2 indicate the amount of data variability explained by the 6-component model. It is possible to observe that the commonalities are typically around 0.90 (90% of the variance of each variable are explained by the 6 factor model). For Hg the communality is 0.89. Although Hg was measured by a different sampler and is mostly in gaseous phase, it was thus possible to explain a high value of 89% of the Hg variance. The last line in Table 2 shows the variance explained for each retained factor. It indicates that the first three factors explain most of the data variability.

The first factor from Table 2 has high loadings for Sc, Sm, La, Th, Ti, Fe, Al, and others. These elements are associated with soil dust aerosol particles. The second factor has high loadings for BC, Mass, S, I, Zn, K, Br and Rb, and it is clearly associated with the biomass-burning
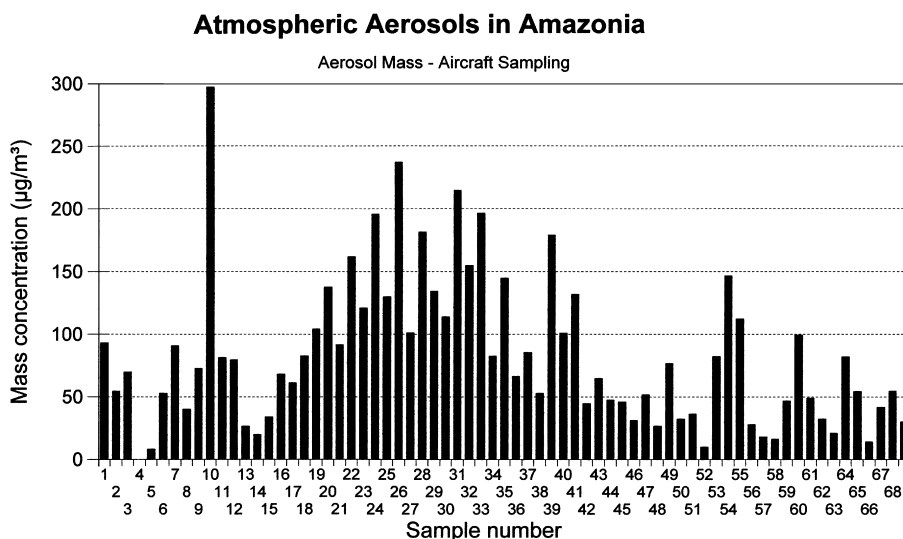
Atmospheric Aerosols in Amazonia

Aerosol Mass - Aircraft Sampling

Fig. 3. Aerosol mass concentration for each sample collected during the SCAR-B experiment in the 1995 dry season Amazon Basin.

Atmospheric Aerosols in Amazonia
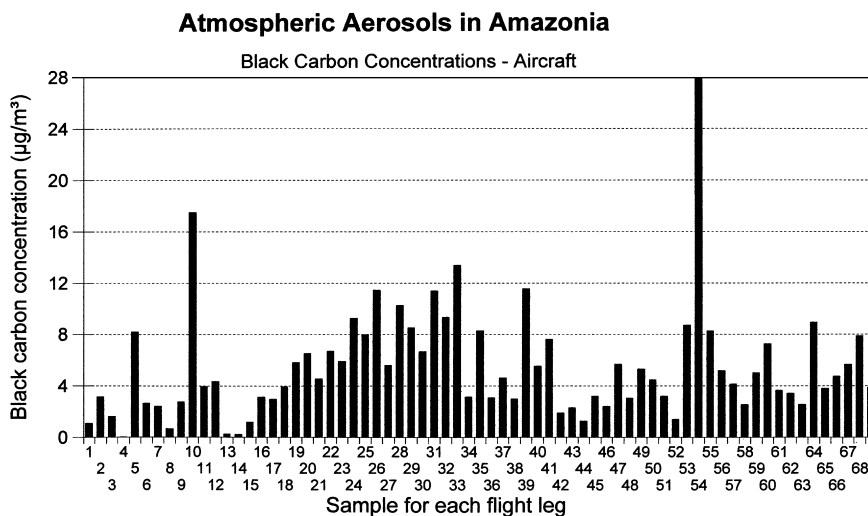
Black Carbon Concentrations - Aircraft

Fig. 4. Black carbon concentrations in $\mu g\,m^{-3}$ for each flight leg during aerosol sampling in the SCAR-B experiment.

component. A low, but statistically significant factor loading of 0.40 for Hg is observed in this biomass-burning component. The third factor has high loadings for Ca, Sr, K, P, Mg, Mn, and because of the associations with P, K, Mg, and the lack of BC, it most likely represents the natural biogenic aerosol. The fourth factor has associations with Ti, Fe, Si, Cu, Rb and others, and is thought to represent a second soil dust component. The flights covered a very large area, and the soil in the Amazon basin could not be called homogeneous over an area of

more than 4 million km². The fifth component has only Na and Cl as elements with significant loadings, and it is associated with intrusions of marine aerosol particles in the Amazon basin. The sixth factor has only Hg with significant loading. This factor is associated with the gold mining activities. Lead was also correlated with this factor, but as lead was not measured in at least 80% of the samples, it was not included in the original factor analysis. The correlation coefficient of Pb with the factor scores of component 6 was a high 0.82. A previous study

Table 2
VARIMAX rotated factor loading matrix for the trace elements, aerosol mass and black carbon in the aerosol phase, together with total Hg[a]

Elements	Soil dust	Biomass burning	Biogenic aerosol	Soil 2	NaCl	Gold mining	Commun.
Sc	0.97	—	—	—	—	—	0.97
Sm	0.97	—	—	—	—	—	0.97
Al	0.97	—	—	—	—	—	0.98
La	0.95	—	—	—	—	—	0.95
Th	0.93	—	—	—	—	—	0.92
V	0.92	—	—	—	—	—	0.89
Ga	0.88	—	—	—	—	—	0.90
Ti	0.75	—	—	0.62	—	—	0.97
Fe	0.72	—	—	0.64	—	—	0.96
BC	—	0.93	0.27	—	—	—	0.96
S	—	0.90	0.26	—	—	—	0.93
I	—	0.87	0.26	—	0.31	—	0.94
Mass	—	0.85	—	—	—	—	0.89
Zn	—	0.76	0.51	—	—	—	0.91
K	—	0.74	0.60	—	—	—	0.93
Br	—	0.72	0.46	—	0.34	—	0.91
Rb	—	0.61	0.41	0.50	—	—	0.91
Ca	—	0.27	0.93	—	—	—	0.95
Sr	—	—	0.91	—	—	—	0.93
P	—	0.38	0.84	—	—	—	0.90
Mg	—	0.35	0.79	—	—	—	0.91
Mn	—	0.47	0.74	—	—	− 0.31	0.91
Cl	—	0.58	0.60	—	0.38	—	0.89
Cu	—	0.38	0.59	0.48	—	—	0.79
Si	0.38	0.32	0.46	0.61	0.26	—	0.90
Na	—	0.34	—	—	0.89	—	0.93
Hg	—	0.40	—	—	—	0.84	0.89
	—	—	—	—	—	—	—
Variance	7.7	6.7	5.8	1.9	1.5	1.2	

[a]Only factor loadings larger than 0.25 are shown. The last column Commun are the communalities of the factor analysis that express the percentage of data variability explained by the 6-factor model for each variable.

of Gerab et al. (1998) using single particle analysis of samples collected directly in gold mining shops in Alta Floresta, observed the strong association between Hg and Pb emissions. In addition, a detailed analysis of factor 6 factor scores shows elevated scores for regions with high gold mining activities in the Amazon basin. Noteworthy with regard to Hg is that it has associations with two factors: the biomass burning component, with a factor loading of 0.40 and the gold-mining component with a factor loading of 0.84. This is an indication that there is some association between total Hg concentration and the biomass-burning aerosol component.

The factor analysis procedure requires normalization of the data matrix to average zero and standard deviation of one. This is done to give identical weights to each variable. A renormalization procedure that retrieves the absolute concentrations can be performed using the absolute principal factor analysis method (APFA)

(Thurston and Spengler, 1985). Fig. 5 shows the absolute source apportionment calculations for mercury. The figure shows the partitioning of Hg for each sample and each retained component. It is evident that most of the Hg is actually associated with the gold mining factor for most of the samples. However, one can also see that the biomass-burning component accounts for the larger part of the Hg in a significant number of samples. There is also a small component of Hg that is associated with the soil dust component, as expected. The Hg amount associated with the natural biogenic component and the sea-salt component is negligible. The background gaseous Hg concentration is probably contained in the biomass burning and gold mining factors. It is very difficult to apportion a rather constant (about 1–2 ng m^{-3}) Hg concentration with this high loading of aerosols, black carbon and ozone in the Amazon basin dry season atmosphere.
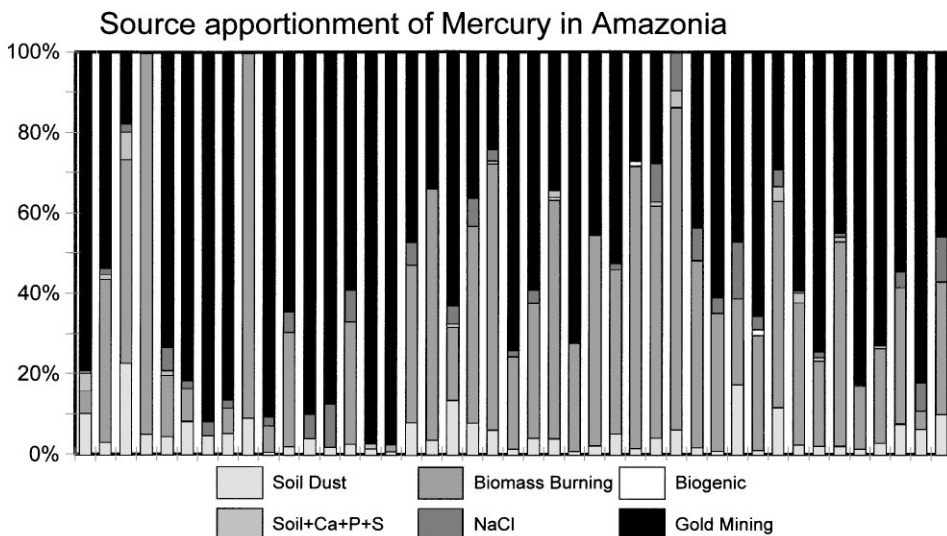
Fig. 5. Mercury quantitative source apportionment for each individual sample for the 6 retained factors.
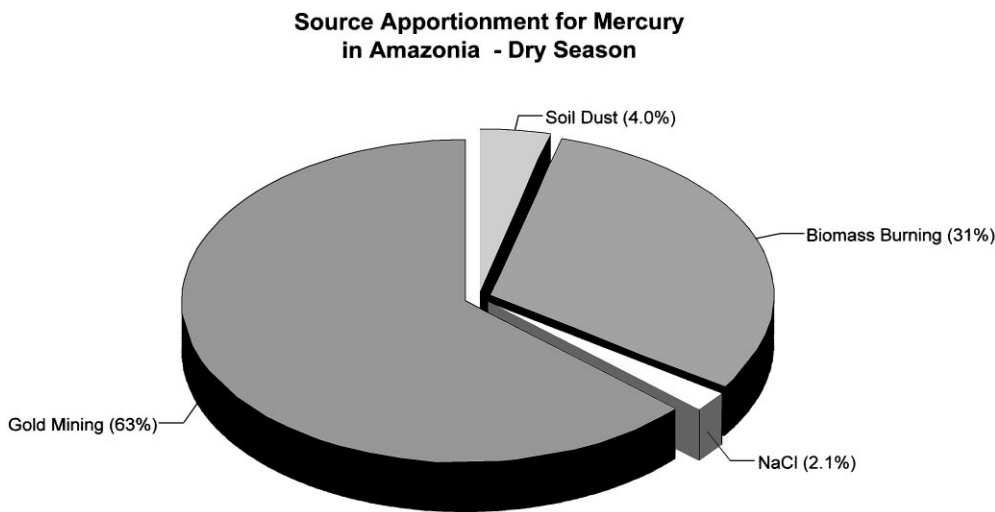

Fig. 6. Quantitative source apportionment for total atmospheric Hg for each factor.

The average quantitative source apportionment for Hg for each component can be observed in Fig. 6. On average, 63% of the Hg is associated with the gold mining activities. A surprisingly high 31% is associated with the biomass-burning component, soil dust accounts for 4% and NaCl for 2.1% of the airborne Hg concentrations. This high association between Hg and biomass burning can be caused by at least three mechanisms: (1) adsorption of gaseous Hg on existing biomass burning particles; (2) direct release of Hg from the vegetation to the atmosphere during forest burning; (3) evaporation of Hg from

soil during the forest burning. The first mechanism could be particularly important, due to the high concentration of fine mode black carbon particles that has a high surface area and strong adsorption properties. The second issue could also play a role, because the Amazon basin soils are relatively rich in mercury, that can be partially be mobilized to the vegetation. However, a lack of data on mercury concentrations in soils and vegetation in the Amazon basin makes it difficult to discuss these mechanisms with confidence. Veiga et al. (1994) discuss the possibility of direct emission of Hg by the vegetation.

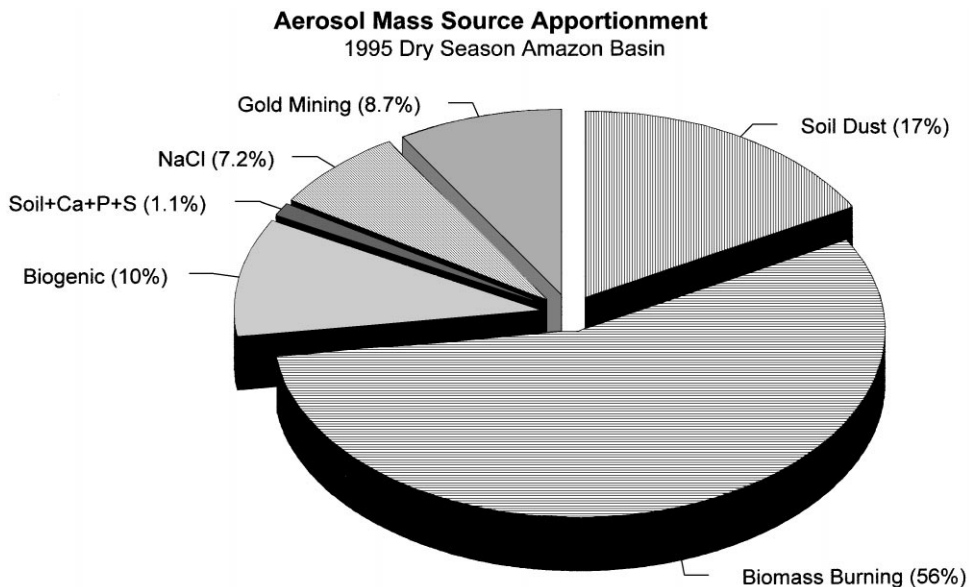**Aerosol Mass Source Apportionment**
1995 Dry Season Amazon Basin

Fig. 7. Aerosol source apportionment for the airborne samples collected in the 1995 biomass-burning season in Amazonia.

The results of our study supports the possibility, but it is not possible to rule out other possible mechanisms of Hg attachment in existing biomass-burning particles.

The aerosol mass source apportionment for particles and mercury in the Amazon basin in shown is Fig. 7. A total of 56% of the aerosol mass is associated with the biomass-burning component, as expected. Soil dust accounts for 17%; natural biogenic aerosol release for 10%; gold mining activities for 8.7%; sea salt for 7.2% and the second soil component enriched in Si accounts for only 1% of the airborne aerosol mass concentration. The 8.7% associated with gold mining activities do not mean that this amount of aerosol mass is directly released by gold mining. During the atmospheric transport, the gaseous Hg can become attached to already existing aerosol particles, and the factor model identifies the two components with similar variability.

Through the APFA procedure it is possible to obtain the absolute elemental source profiles for each retained component. The amount of Hg associated with the gold mining factor is 2.2 ng m^{-3}, and lead is at 2.6 ng m^{-3} in this factor. The ratio of Hg to Pb observed in these airborne samples is similar to the same ratio observed in ground based measurements in Alta Floresta (Hacon et al., 1995).

The long-range transport of the biomass-burning aerosols in South America follows two main pathways: one to the South Atlantic, leaving South America at the 20 to 30° latitude, and the other to the Tropical Pacific, passing over the Andes mountains, near the Equator line (Artaxo et al., 1998; Trosnikov and Nobre, 1998). Remote sensing of aerosol particles with AVHRR and TOMS instruments confirm these two pathways. A similar long-range transport picture applies to atmospheric transport of Hg. Three-dimensional trajectories analysis shows that the South Atlantic pathway can bring Hg and aerosols over very high altitudes, of about 10000 m high (Freitas et al., 1997; Artaxo et al., 1998). With the high atmospheric resident time of Hg, it certainly enters the global circulation through these two long-range atmospheric transport pathways.

4. Conclusions

This paper presents the first large-scale atmospheric mercury measurement experiment in the Amazon basin. Total mercury and aerosol concentrations were measured with three different airplanes covering most of the large area of the Amazon Basin. Mercury concentrations from pristine areas and areas not located downwind from gold mining areas show Hg background values 0.5–2 ng m^{-3}. Over areas that are heavily impacted by gold mining activities or biomass-burning the concentrations of total Hg are 5–14 ng m^{-3}. A factor analysis model of Hg and trace element concentrations resulted in six components. One of these was a factor associated with gold mining activities, with high loadings for total Hg and associated with particulate Pb. There was also an association between total atmospheric Hg and the biomass-burning aerosol component. On average, 63% of the Hg was associated with the gold mining activities. A high value of 31% was associated with the biomass-burning component, soil dust accounted for 4% and an

NaCl factor for 2.1% of the airborne Hg concentrations. The high association between Hg and biomass burning can be caused by at least three mechanisms: (1) adsorption of gaseous Hg on existing biomass-burning particles; (2) direct release of Hg from the vegetation to the atmosphere during forest burning; (3) evaporation of Hg from soil during the forest burning.

Further studies should be designed to clarify these findings. Detailed laboratory studies could be performed with black carbon aerosol particles and gaseous Hg, to obtain transfer factors to the black carbon particles. Also long-term measurement programs for Hg with simultaneous determination of other gaseous and particulate species can be designed to study these particular mechanisms of Hg adsorption on existing aerosol particles.

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