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Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements

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Abstract

Biomass burning is an important global source of aerosol particles to the atmosphere. Aerosol particles were collected in plumes of tropical forest and cerrado biomass burning fires in the Amazon Basin during August–September, 1992. Fine ($d_p < 2 \mu\text{m}$, where d_p is the aerodynamic diameter of the particle) and coarse ($2 \mu\text{m} < d_p < 10 \mu\text{m}$) aerosol particles were collected using stacked filter units. Up to 19 trace elements were determined using particle-induced X-ray emission analysis. Ion chromatography was used to determine up to 11 water-soluble ion components. The dominant species were black carbon, K^+ , Cl^- , and SO_4^{2-} . Organic matter represents in average 70–92% of the fine mode particle mass. The composition of the emitted particles in cerrado fires presents a well-defined pattern related to both the combustion phase and cerrado categories, which is not observed in the case of forest fires. Higher concentrations relative to the fine particulate mass were observed during the flaming emissions compared to the smoldering ones, for almost all experiments. Global emission flux estimates showed that biomass burning could be an important source of heavy metals and black carbon to the atmosphere. Estimates showed that savanna and tropical forest biomass burning could be responsible for the emission of about 1 Gg yr^{-1} of copper, 3 Gg yr^{-1} of zinc and 2.2 Tg yr^{-1} of black carbon to the atmosphere. In average, these values correspond to 2, 3 and 12%, respectively, of the global budget of these species. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Biomass burning; Aerosol particles; Black carbon; Trace elements; Amazonia

1. Introduction

Biomass burning emissions represent an important global source of particles and gases to the atmosphere. Once in the atmosphere, those compounds may alter the properties of the atmosphere since the particles can

absorb and reflect solar radiation (Holben et al., 1991; Andreae, 1991; Kuhlbusch and Crutzen, 1996) and some of the emitted gases such as CO_2 and CH_4 can contribute to the greenhouse effect. Andreae et al. (1996a) have estimated that biomass burning could be responsible for as much as 45% of the global emission of black carbon to the atmosphere, which is highly efficient in absorbing solar radiation (Kuhlbusch and Crutzen, 1996; Martins et al., 1998). Another important feature is that smoke particles can act as cloud condensation nuclei (CCN). This property can be an indirect way of changing the radiation budget of the Earth, in addition to altering the hydrological cycle in tropical regions (Crutzen and Andreae, 1990; Cachier and Ducret, 1991; Hallett et al., 1989; Radke et al., 1991). It was observed that 80–100%

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of the particles emitted during vegetation fires in California could act as CCN (Rogers et al., 1991). Cloud reflectivity is changed with the presence of biomass burning aerosol particles (Kaufman and Nakajima, 1993; Kaufman and Fraser, 1997), which can lead to possible changes in the albedo of tropical regions during the biomass burning season.

Biogeochemical cycles of trace elements in tropical regions may also be changing due to biomass burning emissions. Essential nutrients such as P, S, N, K and others can be exported from the source regions (Goldammer and Crutzen, 1993; Kauffman et al., 1994; Menaut et al., 1993). Emission of heavy metals can cause local and regional pollution of the atmosphere and hydrosphere. During the Chemical Instrumentation Test and Evaluation (CITE 3) experiment, Andreae et al. (1994) observed haze layers over the equatorial and tropical South Atlantic, with elevated concentrations of aerosol particles, O₃, CO and other trace gases related to biomass burning emissions. Analysis of air mass trajectories indicated that the sources of these materials were savanna and grassland fires occurring in Africa and South America, showing the possibility of long-range transport of biomass burning products. Acidification of tropical remote ecosystems may be related to biomass burning because of the significant emissions of acetic and formic acids to the atmosphere (Talbot et al., 1988). Acidification could also occur due to nitric acid formed in the atmosphere via photochemical reactions of NO_x emitted during the fires (Andreae, 1991; Crutzen and Carmichael, 1993; Sanhueza et al., 1991).

The goal of this work was to study the particulate matter (trace elements and ionic constituents) emitted during biomass burning, focusing on the differences in emission of the two main combustion phases: flaming and smoldering. Also, burnings of different vegetation types, which are representative of the Amazon Basin, were studied: basically the cerrado (a savanna-like vegetation) and the tropical rain forest. Global emission fluxes of trace elements and soluble ionic components were calculated to assess the participation of savanna and tropical rain forest biomass burning emissions on the global atmospheric budget.

2. Experimental sites and methods

Aerosol samples were collected at two different sites. Samples from cerrado biomass burning were collected at the IBGE (Brazilian Institute of Geography and Statistics) Ecological Reserve, at 35 km South of Brasília, on the southern limit of the Amazon Basin. A second sampling site was used to collect aerosols emitted during tropical rain forest fires, at Jamari, a small city 100 km South of Porto Velho, in the state of Rondônia.

Cerrado vegetation can be characterized by five different categories (Coutinho, 1978): (1) "campo limpo"; (2) "campo sujo" (tropical grasslands); (3) "campo cerrado" or "cerrado aberto"; (4) "cerrado senso stricto" or "cerrado denso" (savanna); and (5) "cerradão" (forest). In this study, aerosol samples were collected during burnings of "campo limpo", "campo sujo" and "cerrado aberto", which represent the most common types of cerrado in Brazil. "Campo limpo" was the only vegetation grown over a rocky soil. Smoke samples of "campo sujo" and "cerrado aberto" fires were collected in two different months characterizing different fire schedules: the seasonal fires during August (the middle of the burning season) and the late fires of September (last month of the burning season). At the cerrado sites, fire was set on the standing vegetation, while in tropical rain forests, the trees were slashed by the farmers about 20–60 days before burning, to minimize the water content of the biomass. In forest areas, fuels were basically made up of cut wood debris, attached foliage and the litter layer of the forest floor.

Aerosol particles were sampled directly over freshly emitted biomass burning plumes, very close to the sources (about 0.5–2 m away from the fire) to characterize the direct emissions and to avoid effects of aging of the aerosols. A pole about 4 m long was used to help the aerosol sampling. Particles were collected using stacked filter units (SFU) on 0.4 and 8.0 μm pore-sized Nuclepore filters with 47 mm diameter, mounted in series to separate fine ($d_p < 2.0 \mu\text{m}$, where d_p is the aerodynamic diameter) from coarse particles ($d_p > 2.0 \mu\text{m}$) (John et al., 1983). An autonomous and mobile unit composed of a vacuum pump connected to a 12 V battery and a rotameter to monitor the flow rate were used. For cerrado fires, sampling was performed by walking around the burning area, following the source of the plumes. For forest fires, the presence of intact and dense vegetation near the burning area together with the intense heat released by the fires made it very difficult to walk around the burning field and to get close to the sources. The classification criterion for flaming and smoldering emissions was based on the presence of visible flames at the source of the plumes.

Fine and coarse fraction aerosol mass concentrations were obtained by a gravimetric method using an electronic microbalance with 1 μg sensitivity. Details about the procedure are given in Artaxo et al. (1990, 1994). Elemental concentrations were measured by particle-induced X-ray emission (PIXE) analysis (Johansson and Campbell, 1988). Samples were irradiated by a 2.4 MeV proton beam using the PIXE facility at the LAMFI (Laboratório de Análise de Materiais por Feixes Iônicos) laboratory at the University of São Paulo. Details about the experimental PIXE setup, analytical procedures, calibration and uncertainties can be found in Artaxo et al. (1994). The following elements were measured in the

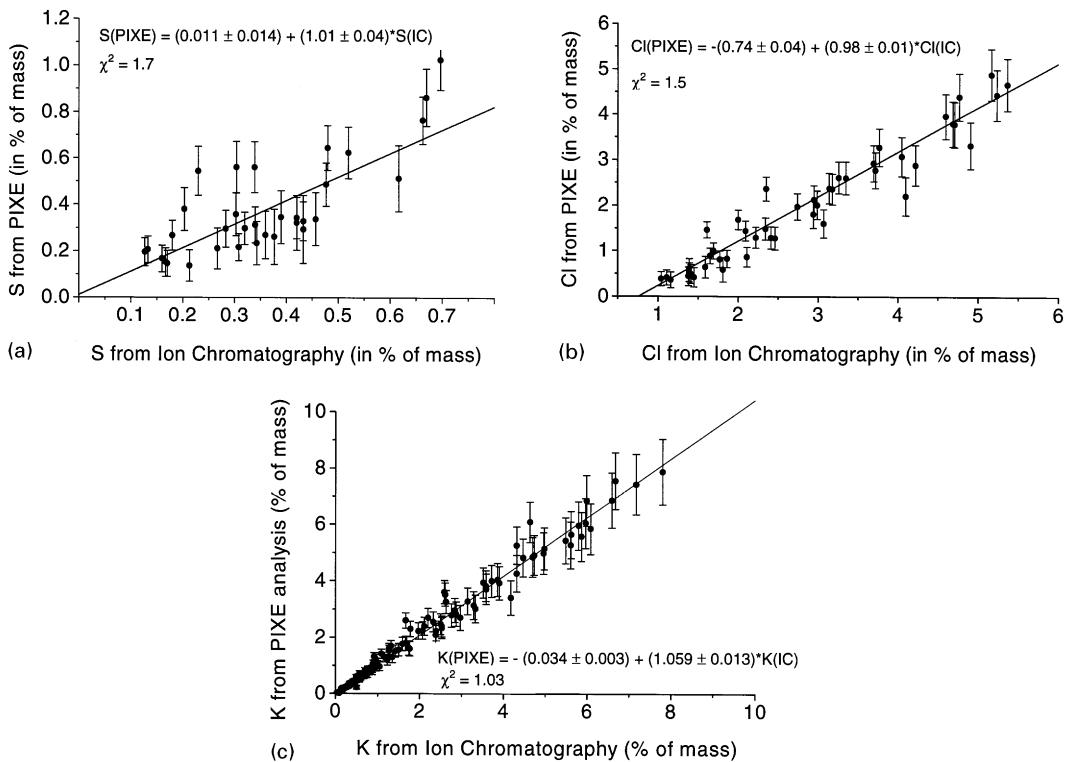


Fig. 1. Comparison between some chemical species concentrations (in percentage of fine particle mass) measured by PIXE and by ion chromatography in samples collected in plumes during direct emission of biomass burning. (a) Sulfur; (b) Chlorine; (c) Potassium.

aerosol samples by PIXE: Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, Rb, Sr and Zr. Black carbon (BC) concentration was determined using an optical reflectance technique (Reid et al., 1998). Ion chromatography was used to determine the water-soluble concentrations of CH_3COO^- , HCOO^- , Cl^- , NO_3^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} as described in Allen and Miguel (1995). Elemental composition, black carbon and water-soluble ionic components are reported only for the fine aerosol mass fraction. This fraction comprises most of the aerosol emissions and corresponds to the most interesting particles for climate change and nutrient cycles studies, due to their long atmospheric residence time and optical properties.

The concentrations for species measured by both PIXE and ion chromatography were compared for internal quality assurance of the data and to study the ratio between soluble and non-soluble and non-volatile components. PIXE measured total elemental concentration, and ion chromatography measured the soluble fraction. Figs. 1a–c show the comparison PIXE versus IC for sulfur, chlorine and potassium concentrations, with slopes ranging between 0.98 to 1.06. The comparison for sulfur was done between total sulfur measured by PIXE

and the fraction of sulfur measured as SO_4^{2-} by ion chromatography. Part of the variability observed for the sulfur comparison in Fig. 1a can be due to the presence of other sulfur compounds present in the samples in addition to (or different from) sulfate. The slopes of Figs. 1b and c show that all Cl and K from biomass burning emissions are mostly water soluble. The result for K is in agreement with Calloway et al. (1989) who showed that 100% of the K released during biomass burning emissions were water soluble. The observed 6% higher potassium in the PIXE results may be related to a small insoluble fraction of K from soil dust resuspension during the combustion process caused by strong atmospheric turbulence.

Principal component analysis (PCA) with VARIMAX rotation was used to study the relationships between the variables (Thurston and Spengler, 1985) for cerrado and forest data independently. Only variables with less than 20% of missing values were considered in the analysis: K^+ , Ac^- (acetate), NO_3^- , Cl^- , SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, BC (black carbon) and FPM (fine particle mass) for cerrado samples. For the aerosol collected in the forest, the same variables were used except for NO_3^- , which presented more than 20% of missing values. Details of the

Table 1

Average composition of chemical species measured in cerrado and tropical forest biomass burning plumes. Results from flaming and smoldering combustion phases are shown^a

Species	Cerrado (% of mass)		Tropical Forest (% of mass)	
	Flaming	Smoldering	Flaming	Smoldering
Ac ⁻	0.28 ± 0.12 (55)	0.25 ± 0.10 (33)	0.25 ± 0.09 (19)	0.26 ± 0.09 (42)
Fo ⁻	0.024 ± 0.012 (54)	0.023 ± 0.013 (33)	0.019 ± 0.009 (13)	0.025 ± 0.014 (29)
Cl ⁻	2.2 ± 1.6 (55)	1.0 ± 1.3 (33)	0.3 ± 0.2 (18)	0.2 ± 0.2 (42)
NO ₃ ⁻	0.62 ± 0.33 (55)	0.33 ± 0.25 (33)	0.12 ± 0.09 (13)	0.12 ± 0.07 (28)
SO ₄ ²⁻	0.72 ± 0.30 (55)	0.35 ± 0.37 (33)	0.90 ± 0.68 (19)	0.39 ± 0.33 (42)
C ₂ O ₄ ²⁻	0.07 ± 0.05 (55)	0.06 ± 0.05 (33)	0.04 ± 0.04 (19)	0.04 ± 0.02 (42)
Na ⁺	0.022 ± 0.016 (39)	0.024 ± 0.021 (20)	0.014 ± 0.008 (16)	0.014 ± 0.009 (26)
NH ₄ ⁺	0.10 ± 0.08 (27)	0.05 ± 0.04 (12)	0.09 ± 0.06 (12)	0.06 ± 0.06 (26)
K ⁺	3.0 ± 2.1 (55)	1.3 ± 1.7 (33)	0.8 ± 0.6 (19)	0.4 ± 0.3 (42)
Mg ²⁺	0.035 ± 0.025 (36)	0.032 ± 0.019 (20)	0.025 ± 0.022 (17)	0.025 ± 0.028 (21)
Ca ²⁺	0.10 ± 0.09 (41)	0.09 ± 0.09 (25)	0.08 ± 0.03 (18)	0.06 ± 0.04 (39)
Al	0.6 ± 0.5 (13)	0.7 ± 1.2 (11)	0.2 ± 0.2 (7)	0.6 ± 0.5 (19)
Si	4.2 ± 1.6 (17)	2.3 ± 1.3 (10)	NM	NM
P	0.052 ± 0.020 (8)	0.042 ± 0.012 (17)	0.045 ± 0.007 (9)	0.036 ± 0.014 (22)
Ti	0.043 ± 0.060 (4)	0.020 ± 0.024 (7)	NM	0.008 ± 0.003 (1)
Cr	0.013 ± 0.002 (2)	0.023 ± 0.021 (3)	NM	0.014 ± 0.005 (5)
Mn	0.009 ± 0.008 (7)	0.006 ± 0.003 (5)	0.005 ± 0.002 (1)	0.003 ± 0.001 (7)
Fe	0.077 ± 0.043 (11)	0.045 ± 0.026 (12)	0.031 ± 0.009 (1)	0.048 ± 0.029 (8)
Ni	0.006 ± 0.002 (1)	0.002 ± 0.001 (3)	NM	NM
Cu	0.005 ± 0.003 (52)	0.004 ± 0.002 (27)	0.004 ± 0.001 (18)	0.003 ± 0.002 (38)
Zn	0.020 ± 0.015 (53)	0.010 ± 0.014 (28)	0.007 ± 0.004 (18)	0.004 ± 0.002 (28)
Se	0.0034 ± 0.0007 (8)	0.0012 ± 0.0003 (6)	0.0028 ± 0.0024 (2)	0.0020 ± 0.0009 (7)
Br	0.057 ± 0.028 (34)	0.042 ± 0.020 (8)	0.051 ± 0.020 (7)	0.029 ± 0.007 (9)
Rb	0.015 ± 0.005 (14)	0.013 ± 0.005 (1)	0.012 ± 0.003 (5)	0.008 ± 0.002 (5)
Sr	0.006 ± 0.004 (4)	0.004 ± 0.002 (7)	NM	0.003 ± 0.002 (1)
Zr	0.018 ± 0.006 (1)	NM	NM	NM
BC	12.6 ± 6.8 (55)	6.5 ± 7.6 (33)	7.3 ± 5.5 (19)	3.9 ± 1.9 (42)

^a Arithmetic mean and population standard deviation are shown. Only values above detection limit were included in the calculations. The number of samples used in the averages is indicated between parentheses. NM means element not measured above analytical detection limits.

procedure are described by Artaxo et al. (1990). Cluster analysis from the standpoint of variables (hereafter called clustering variables) was used to complement principal component results, grouping variables based on their distances from each other on the elemental space. Cluster analysis from the point of view of samples was also applied to group different samples with similar elemental and ionic composition.

3. Results and discussion

This section is comprised of three subsections: discussion of the measured composition in the plumes, according to vegetation type and combustion phases; application of multivariate statistical methods; and estimation of global emission fluxes of some chemical species measured in direct emissions of biomass burning of savanna and tropical rain forest.

3.1. Average elemental and water-soluble species composition

The analysis of the data was performed separating the aerosol samples into four distinct groups according to the sampling classification: (1) samples collected during the flaming phase of cerrado biomass burning; (2) samples from the smoldering phase of cerrado biomass burning; (3) samples from the flaming phase of tropical rain forest biomass burning and (4) samples from the smoldering phase of tropical rain forest fires. Average concentrations, as percentage of aerosol fine particle mass, were calculated for trace elements and ionic components for each group. The results and respective standard deviations are shown in Table 1. For almost all trace elements and water-soluble ionic components, the relative concentrations were higher during the flaming phase (especially for cerrado emissions), suggesting that the organic carbon content is lower in this phase compared to the

smoldering phase. For Cl^- , NO_3^- , SO_4^{2-} , K^+ , NH_4^+ , Zn and black carbon (BC) the relative concentrations in the flaming phase were about twice those of the smoldering phase. These results were observed for both cerrado and forest fires, except for Cl^- and NO_3^- . For these species, the concentrations were higher only for cerrado flaming phase samples. Concerning differences related to vegetation types, relative average concentrations were higher for NO_3^- , K^+ , Zn, BC and particularly for Cl^- , for which the cerrado emissions was about five times higher than in forest biomass burning emissions. Chlorine concentration in vegetation depends strongly on the distance from the coast (McKenzie et al., 1996), due to the contribution of sea-salt aerosol. The wind direction in the Amazon region is predominantly from East (Longo et al., 1999). The Brasília region, where the cerrado biomass burning samples were collected is about 1000 km from the coast, while Jamari (the forest site), is located almost 3000 km from the coast. Andreae et al. (1998) also observed high Cl^- concentrations in a study of savanna fires in Africa. The authors attribute this enrichment to the high halogen content of the semiarid vegetation in the studied region, and also due to the influence of marine aerosol inflow. The observed differences may also be explained by the variability in biomass density, amount of water present in the vegetation before burning and distinct vegetation elemental composition. Tropical rain forest biomass is much denser and wetter than cerrado vegetation and consequently, it burns less efficiently. Acetate and formate showed similar relative concentrations for cerrado and forest fires, with no marked differences observed in any of the two combustion phases.

An estimate of the organic matter fraction was performed as the difference between FPM and the sum of the measured components. In average, the organic matter fraction varied from 70 (during cerrado burning in the flaming phase) to 92% (during forest fire, smoldering phase) of the FPM, with a mean value of 82%. This calculation was performed assuming that Al, Si, Ti and Fe were found basically as oxides: Al_2O_3 , SiO_2 , TiO_2 and Fe_2O_3 , respectively. Cachier et al. (1995) reported that total carbon represents 73% of the total particulate matter measured in direct emissions of savanna fires in Africa and that the carbon-to-oxygen ratio (C/O) may be roughly estimated at about 9. The values in this study are in agreement with these results.

A comparison with data from other authors is presented in Figs. 2, 3a and b, respectively, for cerrado flaming and smoldering phases, tropical rain forest flaming, and tropical rain forest smoldering phase. Data from Ward et al. (1992) were collected using masts of 8–13 m long, in prescribed fires of cerrado vegetation in the IBGE ecological reserve, Brasília, and in prescribed fires of tropical forest vegetation in Marabá, located in the state of Pará, in the eastern Amazon, during the BASE-B experiment, in 1990. Ferek et al. (1998) carried out measurements

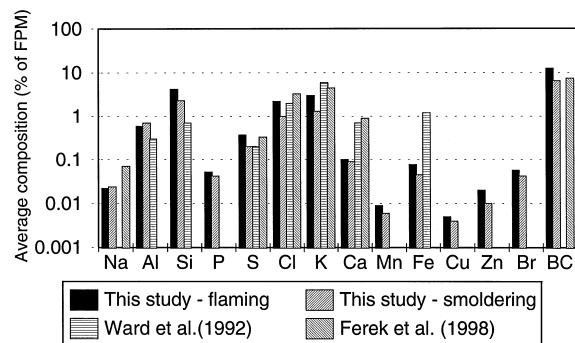


Fig. 2. Comparison of the measured species concentrations (in % of fine particle mass) with data published in the literature. Results for cerrado vegetation biomass burning.

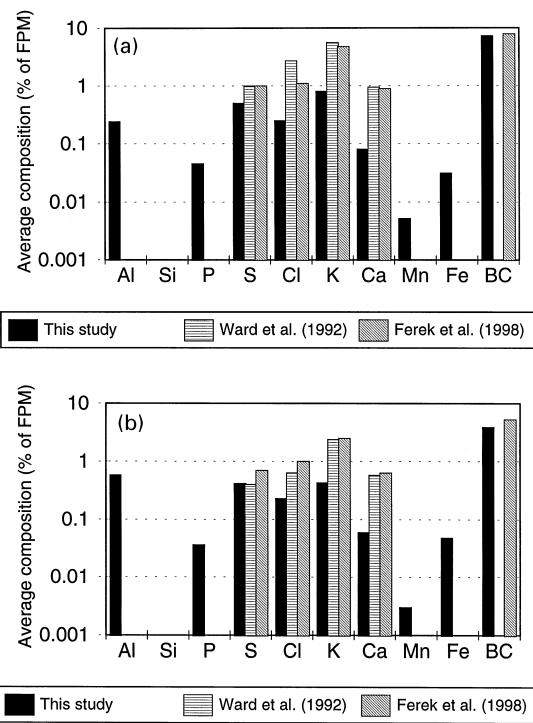


Fig. 3. Comparison of the measured species concentrations (in % of fine particle mass) with data published in the literature. Results for tropical forest under (a) flaming combustion phase; (b) smoldering phase.

in individual plumes aboard the 131-A aircraft in the Amazon region during the SCAR-B experiment, in 1995. For cerrado measurements, it is possible to observe in Fig. 2 that the results from the literature are closer to the flaming phase data of this work, giving indication that they were collected predominantly under flaming phase conditions. For tropical forest biomass burning samples, the results of trace element concentrations from this study are systematically lower than from the other

Table 2

Comparison with results from the literature of elemental mass ratios of potassium, chlorine and sulfur to black carbon, obtained during cerrado fires in Brazil and savanna fires in Africa

This work		Ferek et al. (1998) ^a	Maenhaut et al. (1996) ^b		Andreae et al. (1998) ^c
Flaming	Smoldering		Flaming	Smoldering	
K/BC	0.24	0.20	0.60	0.20	0.17
Cl/BC	0.17	0.15	0.44	0.31	0.22
S/BC	0.029	0.031	0.044	0.021	0.033

^aFrom airborne measurements in Brazil.

^bFrom ground-based measurements in Africa.

^cFrom airborne measurements in Africa, considering only the results for savanna fires.

Table 3

VARIMAX-rotated factor loadings matrix for samples collected in plumes of cerrado biomass burning combustion

Species	Component 1 (Flaming)	Component 2 (Flaming)	Component 3 (Smoldering)	Communality
K ⁺	0.92	0.35	0.00	0.97
Cl ⁻	0.89	0.30	-0.07	0.88
C ₂ O ₄ ²⁻	0.59	0.14	0.70	0.86
SO ₄ ²⁻	0.55	0.80	0.06	0.93
NO ₃ ⁻	0.41	0.53	-0.32	0.56
BC	0.13	0.95	-0.01	0.92
Ac ⁻	-0.03	-0.08	0.96	0.94
FPM	-0.57	-0.10	0.70	0.83
λ	2.80	2.07	2.01	

authors as can be observed in Figs. 3a and b. The differences could be due to the high variability of combustion efficiencies caused by the presence of variable amounts of water in the fuels during the burning. It is important to emphasize that tropical rain forest biomass burnings are expected to present higher variability in the emission factors than cerrado. The burning vegetation in the forest is comprised of leaves and small branches (and therefore are more efficiently burned), to trunks of many centimeters in diameter (which are consumed slower, and can last for many days). Table 2 compares measurements from Brazil with data collected in Africa for savanna vegetation fires. Results from Maenhaut et al. (1996) from ground-based measurements and from Andreae et al. (1998) from airborne measurements of elemental mass ratios of K, Cl and S to black carbon are compared. From the analysis of Table 2 it is possible to observe the similarity of the signatures of cerrado and savanna fire emissions, especially for ground-based samples. Airborne elemental ratios to black carbon are in general higher than ground-based values. The major discrepancies are observed for the results of Andreae et al. (1998) for Cl/BC and S/BC, which are about 5–10 times larger than the results from ground-based measurements. This could also be caused by sea-salt aerosol influences in Southern Africa, especially in airborne samples.

3.2. Application of multivariate statistical methods

The results of principal component analysis (PCA) for cerrado samples showed three components explaining 86.3% of the total data variability. Table 3 shows the component loading matrix after VARIMAX rotation. The three retained components present eigenvalues (λ) higher than 1. The communalities, which indicate the explained fraction of the variability of the measured chemical species, are high for most of the variables. Nitrate was the only variable that presented a low communality (0.56), probably resulting from the high reactivity of nitrate in the atmosphere and from sampling artifacts, either positive (nitrate formation in the filter) or negative (nitrate destruction by reaction with gases or volatilization). Due to these dynamic processes, the variability for nitrate could not be satisfactorily explained by the statistical model. The first component in Table 3 associates mainly K⁺ and Cl⁻ and presents loadings statistically significant also for NO₃⁻, SO₄²⁻, C₂O₄²⁻ and FPM, the latter with negative correlation. In the second component the species BC, NO₃⁻ and SO₄²⁻ are grouped together. The third component aggregates the organic ions CH₃COO⁻ (Ac⁻), C₂O₄²⁻ and FPM. According to Ward and Hao (1991), sulfur, chlorine and potassium contents in the FPM are high during the

Table 4

VARIMAX-rotated factor loading Matrix for samples collected in plumes of tropical forest biomass burning combustion

Species	Component 1 (Flaming)	Component 2 (flaming)	Component 3 (Smoldering)	Communality
SO_4^{2-}	0.86	0.05	0.25	0.80
BC	0.80	0.33	0.09	0.75
K^+	0.43	0.82	0.19	0.89
Cl^-	-0.28	0.88	-0.27	0.92
$\text{C}_2\text{O}_4^{2-}$	-0.05	-0.09	0.94	0.89
Ac^-	-0.80	0.25	0.42	0.87
FPM	-0.81	0.06	0.27	0.74
λ	2.94	1.63	1.31	

higher temperature flaming phase of the fire, and these elements present good correlation with the rate of heat release. Black carbon emissions are also higher during flaming phase (Lobert and Warnatz, 1993; Kuhlbusch and Crutzen, 1996). Therefore, components 1 and 2 may be related to the flaming phase of the combustion. Component 3, on the other hand, appears to be related to the smoldering phase, as the major fraction of FPM is composed of organic compounds (Artaxo et al., 1993, 1998), such as Ac^- and $\text{C}_2\text{O}_4^{2-}$, also present in that component. Nitrate is statistically significant in the two components related to flaming combustion of cerrado. It was observed that nitrogen oxides are released preferentially during flaming combustion (Lobert and Warnatz, 1993). The oxidation of the NO_x emissions could lead to particulate nitrate.

PCA results for emissions of tropical forest biomass burning are presented in Table 4. Three components were statistically significant, explaining 84% of the total variance of the data. The communalities are high for nearly all variables. The relatively low communality of FPM may be related to the high amount of organic compounds present in the samples that could not be traced using the measured variables. For burning emissions from forests, total aerosol mass concentration is higher in smoldering than in flaming conditions (Ward et al., 1992). As organic compounds constitute the major fraction of the particulate matter, the FPM variability depends on how those compounds change from sample to sample. Cerrado emission results showed higher values of communalities for FPM and BC probably because cerrado combustion occurs mainly during flaming phase, resulting in a lower percentage of organic compounds. From these results, the need to better quantify the organic compounds present in biomass burning emissions is evident. PCA results for forest and cerrado are similar: component 1 groups BC, SO_4^{2-} , Ac^- and FPM (the latter two with negative coefficients). Component 2 groups K^+ and Cl^- and the third component groups Ac^- and $\text{C}_2\text{O}_4^{2-}$. Part of component 1 (BC

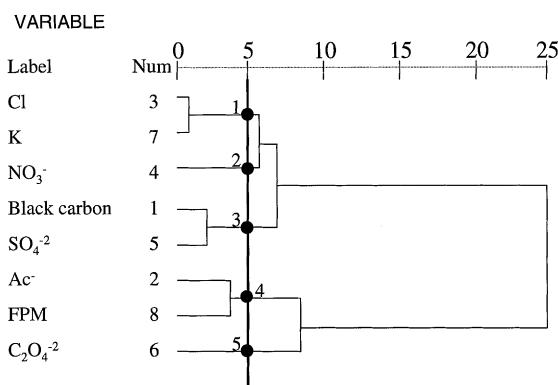


Fig. 4. Dendrogram from cluster analysis showing the grouping of species with similar characteristics for cerrado vegetation fire emissions data set.

and SO_4^{2-}) and component 2 present chemical species emitted mainly during the flaming phase of the combustion, while the other part of component 1 (Ac^- and FPM) and component 3 present chemical species released preferentially during the smoldering phase.

Cluster analyses results (clustering variables) for cerrado and forest data are presented in dendrograms in Figs. 4 and 5, respectively. Although cluster analysis relies on very different statistical methods than PCA, the results are similar. Considering five clusters for cerrado data and four clusters for forest, one can see that for cerrado results, cluster 1 is equivalent to component 1 of the PCA. Cluster 3 corresponds to component 2 and clusters 4 and 5 are related to component 3. The cluster comprising nitrate (cluster 2) is close to clusters 1 and 3, which present chemical species emitted mainly during flaming phase, reinforcing the discussion presented earlier about the possibility of nitrate being formed and released predominantly in the flaming phase. Comparing PCA and cluster analysis results for forest data, it is possible to verify that clusters 1 and 3 are related to

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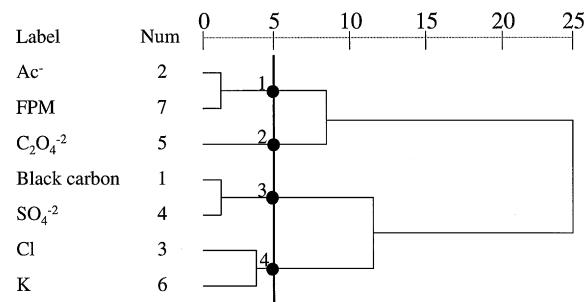


Fig. 5. Dendrogram showing the grouping of species with similar characteristics for tropical rain forest fire emissions data set.

component 1, cluster 2 is equivalent to component 3 and cluster 4 to component 2. Analysis of individual aerosol particles by Gaudichet et al. (1995) and Echalar et al. (1995) showed that most of the potassium and chlorine consists of KCl particles in the smoke plumes. This explains the consistent grouping of K⁺ and Cl⁻ in a component/cluster. Ratios between K⁺ and Cl⁻ concentrations in this study showed an enrichment of about 25% of K⁺ when compared to KCl salt composition. This enrichment may be due to the presence of other potassium compounds or volatilization of chlorine. The presence of groups consisting of BC and sulfate can be the result of adsorption of SO₂ on black carbon particles through the catalytic effect of black carbon particles in the gas to particle conversion of SO₂ to sulfate (Mészáros and Mészáros, 1989; Novakov et al., 1974; Novakov, 1984). This effect occurs in two distinct stages, the first one in a very fast way (few seconds to minutes) allowing sulfate formation relatively close to the source (Novakov, 1984). According to Novakov et al. (1974), the presence of oxygen in air is important for SO₂ oxidation and high relative humidity enhances the effect. The flaming phase combustion of biomass burning demands oxygen concentrations of about 15% or higher, and during this phase, water vapor is released from the vegetation fuel, with the emission of black carbon and SO₂ (Lobert and Warnatz, 1993). Therefore, flaming conditions present an appropriate environment for the occurrence of sulfate formation on black carbon particles and the multivariate statistical analysis results of this study corroborate this hypothesis.

Clustering of cases was used to distinguish similar structures among samples. The results are presented in the graphs shown in Figs. 6 and 7, where cluster numbers are indicated in the vertical axis and the sample identifications in the horizontal. It is possible to observe a separation of samples according to combustion phase and different vegetation types for cerrado results. Cluster 1 groups mainly samples collected during smoldering phase of "campo sujo" burnings. Clusters 2 and 3

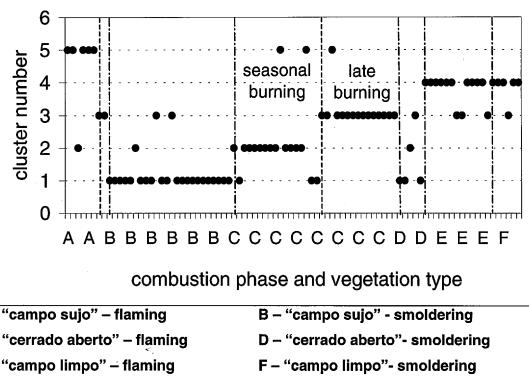


Fig. 6. Cluster analysis results (clustering cases) for cerrado biomass burning emissions in the fine mode, grouping samples with similar characteristics. Vertical bars were included to facilitate visualization: separating vegetation types, combustion phases, and distinct clusters, in particular to emphasize the separation by the method of samples collected in different burning periods.

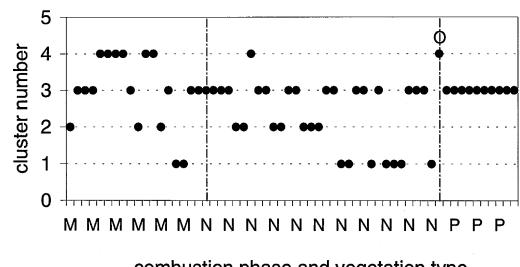


Fig. 7. Cluster analysis results (clustering cases) for tropical rain forest biomass burning emission in the fine mode, grouping samples with similar characteristics.

separate samples collected during flaming phase of "cerrado aberto" fires. Cluster 5 shows samples from "campo sujo" flaming fires and cluster 4 isolates samples collected during "campo limpo" fires. In the latter case, there was no separation relating to combustion phase. The "campo limpo" vegetation is dominated by grasses without trees or shrubs and was the only one that has grown on a rocky soil. Clusters analysis results showed also a distinction between samples collected in different fire schedules. Cluster 2 refers to samples collected during seasonal fires (in August) and cluster 3 to samples from late fires (in September). This result may be a demonstration that the combustion process depends on the amount of water present in the biomass before burning, since the water content is expected to be lower in September, the last month of the burning season.

Table 5

Values of combustion efficiency (CE), fraction of biomass consumed in each combustion phase (P), fine particulate matter emission factor (ef) and global fine particulate matter emission fluxes (F) used in the estimation of global emission fluxes for some chemical species emitted by savanna and tropical forest biomass burning

Vegetation type	Combustion phase	Combustion efficiency (CE) ^a	% of biomass burned in each phase (P) ^a	ef(FPM) (g kg ⁻¹)	F(FPM) (Tg yr ⁻¹)
Savanna	Flaming	0.94	0.90	3.25	10.8
	Smoldering	0.90	0.10	6.09	2.2
Forest	Flaming	0.90	0.20	6.09	2.6
	Smoldering	0.87	0.80	8.22	13.8

^aBased on results of Ward et al. (1992).

Fig. 7 shows the cluster results for the forest samples. The results from the clustering of forest samples show a more complex structure, not necessarily related to the combustion phase. One can see that all samples collected during smoldering phase of secondary forest fires have been grouped in cluster 3. The difficulty of sample separation may have resulted from the vegetation complexity. Tropical rain forest is composed of trees with trunks and branches covering a wide range of diameters, which results in different degrees of dryness, according to their structures. There were also several logistical problems of sampling forest fires from the ground. As the forest burning areas were surrounded by intact vegetation, sampling was performed at isolated points which can cause some sampling artifacts, as discussed previously in Section 2. The heat released by the fires did not allow a closer approximation of the plume sources, resulting in a mixing between plumes of distinct combustion phases. In addition, the height of the fires makes it difficult to collect samples of flaming phase of forest fires from the ground. Finally, Andreae et al. (1998) suggest that ground-based sampling is limited to the less vigorous part of the forest fire.

3.3. Global emission fluxes estimation

Global emission flux estimates of some chemical species from savanna and tropical forest fires can be performed using the measured emission profiles. The mathematical expression used to perform the estimates was

$$F(X) = \frac{M(X)}{M(FPM)} \times F(FPM), \quad (1)$$

where $F(X)$ is the global emission flux of the chemical species X emitted annually due to savanna or forest fires (Tg yr⁻¹), $M(X)/M(FPM)$ is the concentration of the chemical species X relative to the fine particulate matter concentration, whose value is presented in Table 1, $F(FPM)$ is the global emission flux for fine particulate

matter (in Tg yr⁻¹), estimated according to the procedure of Ward and Hao (1991), based on the fine particulate matter emission factor, ef(FPM) (in g kg⁻¹), as a function of combustion efficiency (CE) (Ward et al., 1992):

$$ef(FPM) = 69.9 - 70.9(CE). \quad (2)$$

The global annual emission flux for the fine particulate matter ($F(FPM)$) is the product of ef(FPM) and the total biomass burned annually (T_b). The values used for T_b were adapted from Hao et al. (1990) as 3690 Tg yr⁻¹ for savanna and 2100 Tg yr⁻¹ for tropical forest. The value for tropical forest was obtained considering a combustion factor of 50% (Ward et al., 1992), instead of the 30% used originally by Hao et al. (1990). Another correction refers to the fractions of the total biomass consumed under flaming and smoldering conditions (P). Thus, the annual emission flux for the fine particulate matter according to the vegetation type and combustion phase is given by

$$F(FPM) = ef(FPM) \times T_b \times P, \quad (3)$$

Table 5 presents the values of CE, for each vegetation type and combustion phase used to calculate ef(FPM), P , and $F(FPM)$. Values of combustion efficiency and corresponding fraction of biomass consumed in each phase are based on the results of Ward et al. (1992), since those variables were not quantified in the present study. Although the values from Ward et al. (1992) refer to distinct field campaigns in the Amazon region, it is assumed that, in average, those values are representative of cerrado and forest fires in general. Comparison of FPM emission fluxes from this study (13.0 Tg yr⁻¹ for savanna fires and 16.4 Tg yr⁻¹ for tropical forest — Table 5) with those estimated by Ward and Hao (1991) (19.4 Tg yr⁻¹ for savanna and 12.8 Tg yr⁻¹ for tropical forest) demonstrates the importance of making the apportionment of the consumed biomass according to the distinct combustion phases. This shows that, actually, contributions of tropical forest fires to the emission of FPM are greater than those of savanna fires.

Table 6

Global emission fluxes for some chemical species, in Gg yr⁻¹ (1 Gg = 10⁹ g), by savanna and tropical forest biomass burning

Species	Global emission fluxes (Gg yr ⁻¹)				
	Savanna		Tropical forest		
	Flaming	Smoldering	Flaming	Smoldering	Total
Ac ⁻	30 ± 13	6 ± 2	7 ± 2	36 ± 12	79 ± 18
Fo ⁻	2.6 ± 1.3	0.5 ± 0.3	0.5 ± 0.2	3.5 ± 1.9	7.1 ± 2.3
SO ₄ ²⁻	80 ± 30	8 ± 8	20 ± 20	50 ± 50	160 ± 60
K ⁺	320 ± 230	30 ± 40	20 ± 20	60 ± 40	430 ± 240
P	5.6 ± 2.2	0.9 ± 0.3	1.2 ± 0.2	5.0 ± 1.9	12.7 ± 0.9
Mn	1.0 ± 0.9	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.1	1.6 ± 0.9
Cu	0.54 ± 0.32	0.09 ± 0.04	0.10 ± 0.03	0.41 ± 0.28	1.14 ± 0.43
Zn	2.2 ± 1.6	0.2 ± 0.3	0.2 ± 0.1	0.6 ± 0.3	3.2 ± 1.7
Br	6.2 ± 3.0	0.9 ± 0.4	1.3 ± 0.5	4.0 ± 1.0	12.4 ± 3.2
BC ^a	1.4 ± 0.7	0.1 ± 0.2	0.2 ± 0.1	0.5 ± 0.3	2.2 ± 0.8

^aGlobal emission fluxes for BC (black carbon) in Tg yr⁻¹ (1 Tg = 10¹² g).

Emission fluxes for some chemical species were calculated using Eq. (1) and the values from Table 5. The results are presented in Table 6. Echalar et al. (1995) and Andreae et al. (1996a) performed similar estimates for savanna fires. Andreae et al. (1996a) found values of 19 Tg yr⁻¹ for the FPM emission flux (similar to the result of Ward and Hao, 1991), 3 Tg yr⁻¹ for black carbon and 1.2 Tg yr⁻¹ for potassium. Echalar et al. (1995) also reported an emission flux for potassium of 1.2 Tg yr⁻¹. The estimates from this work are lower: 1.5 Tg yr⁻¹ and 0.35 Tg yr⁻¹, for black carbon and potassium, respectively. The observed discrepancies are probably due to the lower ef(FPM) from this work (combustion phase-weighted average of 3.5 g kg⁻¹ compared to the 5 g kg⁻¹ obtained by Andreae et al. 1996a), and lower BC and K concentration in percent of mass observed in this study. The presence of bromine in the particulate phase suggests the investigation of Br in the gas phase as CH₃Br. According to Manö and Andreae (1994), this compound is much more efficient on a per atom basis than CH₃Cl in breaking down ozone, and could be responsible for a significant fraction of the global ozone layer depletion. According to Andreae et al. (1998) about 78% of the bromine emitted during savanna fires are in the particulate phase. Andreae et al. (1996b) estimated a global emission flux of CH₃Br of 6.8 Gg yr⁻¹, which corresponds to an emission flux of 5.7 Gg yr⁻¹ of Br in the gas phase. The emission flux estimate from this work for bromine in the particulate phase was of 7.1 Gg yr⁻¹ from global savanna fires. Combining these values, it follows that 55% of Br could be released as aerosol particles during savanna fires, which is of the same order of magnitude from the estimate of Andreae et al. (1998). Estimated emission fluxes

Table 7

Fraction attributed to savanna plus tropical forest fires in the global anthropogenic balance of emissions^a

Species	Percentage
Mn	5% (2–8)
Cu	2% (1–3)
Zn	3% (2–4)
BC	12% (8–16)

^aNumbers in parentheses indicate the lowest and highest values, respectively.

for Mn, Cu and Zn are compared with values from the assessment of anthropogenic emissions of heavy metals made by Nriagu and Pacyna (1988). Table 7 shows the percent contribution of savanna plus tropical biomass burnings in the global emissions of Mn, Cu and Zn. In the same table, the percentage attributed only to savanna and tropical forest biomass burnings in the global emission of black carbon (BC) is shown, taking into account all possible sources (Andreae et al., 1996a). Local and/or regional impacts could be more intense, since biomass burning prevails mainly in areas where industrial activities are still scarce.

4. Conclusions

Concentrations for potassium, zinc and black carbon, in percentage of mass, were higher during the flaming phase of both cerrado and tropical rain forest fires. Considering different vegetation, cerrado burnings were

enriched in NO_3^- , Zn, black carbon and Cl^- , when compared to forest fires. Emission ratios for organic ions were similar in all studied cases, showing that they vary alike the fine mode mass concentration, since it is composed mainly of organic matter. Multivariate statistical analyses (principal component and cluster analyses) were helpful in characterizing trace elements and ionic components emitted from biomass burning. It was possible to observe a grouping of K^+ and Cl^- resulting from the formation of KCl during the burning processes, preferentially in the flaming phase of the combustion. Black carbon and sulfate presented similar variability, possibly due to the catalytic effect of black carbon particles in the gas-particle conversion process of SO_2 to sulfate. According to the results from the present study, it can be inferred that nitrate appears preferentially during the flaming phase of biomass burning combustion because of the similar variability with chemical species released mainly during that phase (BC, SO_4^{2-} , K^+ and Cl^-).

Cerrado biomass burning presents a well-defined pattern of emission in terms of combustion phase and cerrado categories. Tropical rain forest results, on the other hand, were difficult to interpret, resulting in structures not related to combustion phase or forest type (primary or secondary tropical forest). This can be a result of sampling difficulties. Another possibility is the variety of vegetation species in tropical rain forest, constituted of trees with large trunks, leaves and small branches which demand different times to dry and to burn, with different efficiencies.

During biomass burning there is a significant emission of acidic organic components (acetate, formate and oxalate), with possible acidifying effects in the Amazon ecosystem. Most of the aerosol particles were water-soluble, showing the potential role of biomass burning in changing CCN particle number and composition. These changes could alter cloud formation mechanisms and albedo, consequently changing atmospheric radiative processes and water cycles in tropical regions. Significant amounts of organic matter and black carbon substances are emitted, especially during cerrado fires under flaming phase conditions. Black carbon has strong radiation absorption that can change the temperature vertical profile in regions with intense biomass burning. Concerning the transport of essential plant nutrients and the emission of heavy metals, emission flux estimates showed a significant contribution of savanna and tropical forest fires to the biogeochemical cycles of these species, in a global perspective.

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