Nuclear Instruments and Methods in Physics Research B49 (1990) 366–371
North-Holland

TRACE ELEMENT CONCENTRATIONS AND SIZE DISTRIBUTION OF BIOGENIC AEROSOLS FROM THE AMAZON BASIN DURING THE WET SEASON

Paulo ARTAXO

Instituto de Física, Universidade de São Paulo, Caixa Postal 20516, 01498 São Paulo, SP, Brazil

Willy MAENHAUT

Institute for Nuclear Sciences, Rijksuniversiteit Gent, Proeftuinstraat 86, B-9000 Gent, Belgium

Atmospheric aerosols were sampled in the tropical rain forest of the Amazon Basin during April and May, 1987 (wet season) as part of the NASA Global Tropospheric Experiment (GTE), during the Amazon Boundary Layer Experiment (ABLE-2B). A special fine particle aerosol sampler and 6-stage single orifice cascade impactors were used for the aerosol collections. The samples were analyzed for 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Br, Rb, Sr, Zr, and Pb) by particle-induced X-ray emission (PIXE). Absolute principal factor analysis was used to interpret the fine particle aerosol elemental concentrations, and to obtain elemental source profiles. The concentrations of the fine mode soil dust related elements (Al, Ti, Mn, and Fe) were more than 10 times larger in the wet season than in the dry season. The biogenic aerosol related elements (e.g. P, S, K, and Zn) in the fine mode showed strongly reduced concentrations in the wet season. Sulphur concentrations averaged 92 ± 54 ng/m^3 in the fine mode aerosol. The concentrations of soil dust related elements were 80% higher during daytime than during night, whereas the biogenic related elements showed much lower levels during day than during night. Two factors explained more than 92% of the data variability for the day and night fine particle samples. These factors were soil dust (represented mainly by Al, Si, Ti, Mn, and Fe) and biogenic related aerosol (with K, P, S, and Zn). Source profiles were obtained for the fine mode aerosol, and the soil dust factor had a similar elemental composition as average crustal rock. The size distributions of the soil dust related elements, as measured at three different levels (ground level, 28 and 45 m), were very similar, whereas for the biogenic related elements some differences as a function of height were observed. The sulphur size distribution was clearly bimodal, but the fine mode was significantly reduced at ground level. Considering the concentrations measured in this work and the large area of the tropical rain forests, biogenic aerosol particles can play an important role in the global aerosol budget and in the global biogeochemical cycles of various elements.

1. Introduction

It is since long recognized that tropical rain forests have a major impact on global weather and climate. Particularly the Amazon Basin, with approximately 4 million square kilometers, plays a very important role in emissions of water vapor, gases and aerosol particles to the atmosphere [1,2]. The intense convective activity [3] results in rapid vertical mixing of biogenic gases and aerosol particles to high altitudes where they can be transported over long distances and have an impact on global tropospheric chemistry [4,5]. Atmospheric aerosols from forested regions are also important in the biosphere-atmosphere cycling of C, N, S, P, and several other essential plant nutrients. Despite their importance, only few studies of the aerosol elemental composition and particle size distribution have been conducted in these environments [6–14]. Studies of aerosol emissions during the burning of forests have been carried out at several locations [15], including the Amazon Basin [11,16]. These studies indicate that large amounts of the fine mode aerosol particles and gases are emitted to the atmosphere by forest burning in the South American and African rain forests. In the present study, the natural emission of aerosols by the vegetation was investigated.

The forest is a profile source of natural aerosols, both during the dry and wet season. Fish [17] and Crozat [18] have hypothesized that the natural release of particles by the vegetation is a major natural global source of aerosols. Decaying vegetation can generate small particles that act as cloud nuclei [19]. Large biogenic particles can be produced by mechanical abrasion [20] or the release of windblown pollen grains [21]. Curtin at al. [22] found Na, Mg, Mn and Zn in exudates from conifer trees. In West Africa, Crozat [18] observed potassium enrichment in biogenic aerosol. Artaxo [9] and Artaxo and Orsini [23] studied the aerosol elemental composition in the Brazilian Atlantic forest. They observed that the biogenic aerosol source profiles, as derived from receptor modelling, were similar to the ones obtained in the dry season in the Amazon Basin.

The data presented in this paper were obtained during the wet season in central Amazonia, Brazil, as

0168-583X/90/$03.50

part of the NASA Global Tropospheric Experiment (GTE)–Amazon Boundary Layer Experiment (ABLE-2B) conducted in April/May 1987 [24]. ABLE-2B was a large experiment involving aerosol and gas sampling with the NASA Electra aircraft, boat sampling along the Negro and Amazonas rivers, and ground based sampling at four remote sites with 45 m high meteorological towers inside the jungle. Extensive meteorological measurements were also performed. The paper by Artaxo et al. [14] gives a full description of the aerosol composition data obtained from sampling with stacked filter units at the various sampling sites. In this paper, data obtained with a special fine mode aerosol sampler and cascade impactors will be presented.

2. Experimental methods

2.1. Sampling sites and procedures

The sampling sites were located in the central part of the Amazon Basin, in the Ducke Forest Reserve (2°56′02″S; 59°57′41″W; elevation 120 m above MSL) near the city of Manaus. Two sampling sites were used: the 45-m-high tower in the Ducke Forest Reserve and the Ducke Meteorological site. The distance between the two sites is about 3 km and the forest around both sites is virginal and undisturbed. In the tower, cascade impactors samples were collected at three levels – top level: 45 m high; forest canopy level: 28 m high; and ground level. The forest canopy itself is at about 35 m height. The dominant wind direction (over 90% of the time) was northeast to east, so that the urban plume of the city of Manaus could not reach the sampling sites for most of the time. High resolution (5 min) wind direction and wind velocity measurements were carried out at NCAR PAM stations. Temperatures during the sampling campaign were between 22 and 34°C. During April and May we had only 5 days without precipitation in the area of the sampling sites. Forest burning did not occur in the Amazon Basin during the experiment, as deduced by the ABLE-2B meteorological team from satellite pictures and aircraft observations.

Aerosols were sampled using a special fine particle sampler (FPS), consisting of a cyclone to collect coarse particles and a 0.4 μm pore size Nuclepore filter. The cyclone has a 50% cutoff diameter of 2.0 μm at a flow rate of 15 lpm. The Nuclepore filter collects the fine particles in a small 0.8 cm^2 area that makes it ideal for PIXE analysis. The air volume was measured with a calibrated linear mass flowmeter. The sampling time was 12 hours, allowing the collection of separate daytime and nighttime fine mode aerosol samples. Filters were changed at about 7 a.m. and 7 p.m. every day from April 6 to May 15, 1987. All FPS collections took place at the Ducke Meteorological site. The aerosol size distribution was measured with a 6-stage single orifice Battelle-type cascade impactor (CI) (PIXE International Corporation, Tallahassee, Florida). At a flow rate of 1 lpm the 50% cutoff diameters for the cascade impactor stages 5, 4, 3, 2, and 1 are: 4, 2, 1, 0.5 and 0.25 μm. A Nuclepore backup filter collects particles smaller than 0.25 μm. Vaseline coated Kimfol polycarbonate film was used as impaction surface in stages 5 to 2, and paraffin coated Mylar film was used in stage 1. A 0.4 μm Nuclepore filter served as backup filter. The sampling time for the CI was about 24 hours.

2.2. PIXE analysis

The aerosol elemental concentrations were measured by particle-induced X-ray emission (PIXE) [25]. The samples were irradiated by a 2.4 MeV proton beam, supplied by the isochronous cyclotron of the University of Gent. Full details about the experimental PIXE setup, analytical procedures, calibration, and uncertainties are given elsewhere [26,27]. The X-ray spectra were fitted by the AXIL program, and concentration data were obtained for the following 24 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Br, Rb, Sr, Zr, and Pb. However because of its soft X-ray energy, the data for Na should be considered as semi-quantitative only.

3. Absolute principal factor analysis

As we were interested in identifying the natural sources of aerosols in the Amazon Basin and in extracting their elemental source profiles, the elemental concentration data were analyzed by absolute principal factor analysis (APFA) [28]. In APFA, we start by constructing a model of the variability of the trace element concentrations, so that the set of intercorrelated variables is transformed into a set of independent, uncorrelated variables. This is done by calculating the eigenvectors and eigenvalues of the correlation matrix of elemental concentrations [29]. The most prominent eigenvectors (factors) are retained and orthogonally rotated by a VARIMAX rotation [30]. A "factor loading matrix" then represents the correlations between the trace elements and each orthogonal factor, and "factor scores" can be calculated which indicate the relative importance of each factor for each individual sample [31,32]. A renormalization procedure [28] allows one to obtain the "absolute principal factor scores" (APFS) for each sample. The observed atmospheric concentrations are subsequently regressed on the APFS. This results in source profiles with elemental compositions for the particles emitted by each source.

4. Results and discussion

It is important to emphasize that the biogenic aerosol component discussed in this paper is not related to biomass burning, but to the natural release of aerosols by the vegetation. No forest burning occurs in the wet season because of the very high precipitation rate. Table 1 shows the wet-season average elemental concentrations for the fine particles collected in the Ducke Reserve sampling site. To allow a comparison between the wet and dry season elemental concentrations, the last column presents the average fine mode elemental concentrations measured in the 1985 dry-season experiment (ABLE-2A) [13]. A comparison for the fine particle soil dust related elements (e.g. Al, Ti, Fe) shows that the average concentrations of these elements are much higher during the wet season than during the dry season. This surprising result is due to the different meteorological conditions, that had for effect that there was an influx of long range transported soil dust to the Amazon Basin during the wet season [33,14]. Meteorological data and trajectory analysis pointed to the Sahara desert as the probable source region for this long range transported soil dust [34,33]. Table 1 also shows that the biogenic related elements (e.g. K, P, S) exhibited much lower elemental concentrations in the fine mode during the wet season than during the dry season. This reduction can be due to less active plant metabolism for production of fine mode aerosols. Other observations from table 1 are that the soil dust related elements exhibited 80% higher levels during daytime than nighttime, whereas the biogenic related elements showed higher concentrations during nighttime. This probably occurred because of differences in the height of the boundary layer, which during daytime extended up to about 800 m, whereas during nighttime it was restricted to just above the forest canopy [36]. The sulphur concentration was reduced by a factor of 3 in the wet season compared to the dry season. The much higher rainfall and the consequently higher scavenging rate of fine mode sulphur particles can be partially responsible for this difference.

Table 1
Average fine mode aerosol elemental concentrations in ng/m^3 for the ABLE-2B experiment during the wet season in the Amazon Basin [a]

Element	Day	Night	Dry season
Na	96.5 ± 43.2	54.8 ± 20.0	–
Mg	46.4 ± 33.3	27.4 ± 22.3	11.9
Al	186 ± 229	101 ± 140	8.37
Si	399 ± 522	222 ± 327	–
P	18.2 ± 7.9	38.8 ± 14.0	3.87
S	97.5 ± 57.1	86.3 ± 46.3	259
Cl	18.4 ± 18.8	12.0 ± 9.6	6.06
K	81.8 ± 57.6	107 ± 42	161
Ca	45.1 ± 56.9	23.1 ± 26.2	3.94
Ti	12.8 ± 15.3	7.51 ± 10.3	0.89
V	0.64 ± 0.19	0.51 ± 0.21	1.14
Cr	1.19 ± 0.58	1.15 ± 0.58	0.76
Mn	2.08 ± 2.26	1.21 ± 1.38	0.30
Fe	101 ± 131	60.2 ± 84.1	6.53
Ni	0.55 ± 0.16	0.36 ± 0.19	0.54
Cu	0.33 ± 0.16	0.28 ± 0.11	0.36
Zn	1.02 ± 0.43	1.49 ± 0.63	1.61
Ga	0.12 ± 0.06	0.13 ± 0.13	–
Se	0.23 ± 0.14	0.12 ± 0.06	–
Br	1.06 ± 0.30	0.69 ± 0.24	0.95
Rb	0.53 ± 0.34	0.40 ± 0.21	0.52
Sr	1.01 ± 0.79	0.71 ± 0.58	–
Zr	1.98 ± 0.31	0.62 ± 0.48	–
Pb	0.55 ± 0.17	0.57 ± 0.21	0.73

[a] The column "Day" presents averages ± standard deviations for 25 samples collected during daytime, and the column "Night" gives averages for 25 nighttime samples. Data for Na should be considered as semi-quantitative only. To allow a comparison between the wet and dry season elemental concentrations, the last column presents the average concentrations for fine mode aerosol samples from the 1985 dry season experiment (ABLE-2A).

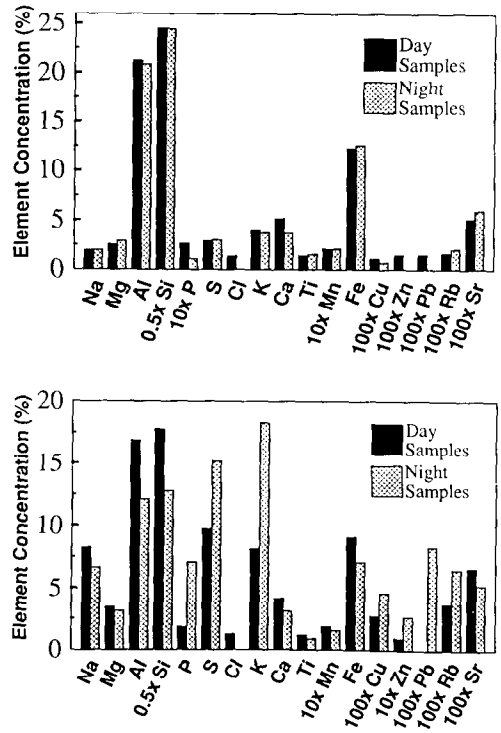

Fig. 1. Elemental source profiles obtained by absolute principal factor analysis for the fine mode components of the Amazon Basin aerosol. Concentrations are normalized to the sum of the measured trace elements (top: soil component profiles, bottom: biogenic component profiles).

Table 2
Principal factor analysis results for the fine mode aerosol from the ABLE-2B experiment during the wet season in the Amazon Basin. Fine mode aerosol particles collected at the Ducke Meteorological site [a)]

Factor	Eigenvalue Structure			
	Day samples ($m = 12$; $n = 25$)		Night samples ($m = 12$; $n = 25$)	
	λ	%	λ	%
1	10.46	86.9	8.80	72.9
2	0.79	93.5	2.30	92.0
3	0.42	97.0	0.45	95.8
4	0.27	99.2	0.26	97.9
5	0.04	99.6	0.15	99.1

Element	Day samples			Night samples		
	Factor loadings		Communalities	Factor loadings		Communalities
	Soil	Plant		Soil	Plant	
Mg	0.77	0.63	0.99	0.97	0.21	0.98
Al	0.91	0.42	0.99	0.98	0.18	0.99
Si	0.92	0.40	0.99	0.98	0.16	0.99
P	0.30	0.88	0.87	0.03	0.95	0.91
S	0.50	0.72	0.78	0.40	0.79	0.78
Cl	0.83	0.50	0.95	0.71	0.48	0.74
K	0.69	0.69	0.95	0.60	0.76	0.94
Ca	0.89	0.44	0.99	0.96	0.25	0.99
Ti	0.91	0.42	0.99	0.98	0.15	0.99
Mn	0.89	0.45	0.99	0.97	0.19	0.98
Fe	0.91	0.42	0.99	0.98	0.15	0.99
Zn	0.38	0.78	0.75	0.05	0.90	0.82

[a)] m is the number of variables in the factor analysis calculations; n is the number of samples. λ is the eigenvalue associated with each factor, and % indicates the cumulative percentage of explained variance.

Principal factor analysis (PFA) was performed separately for the daytime and nighttime samples in order to investigate the differences in associations of the different elements between day and night. Table 2 presents the eigenvalue structure and the VARIMAX rotated factor loading matrix. For both daytime and nighttime samples only 2 factors are statistically significant, and they explain 93.5 and 92% of the data variability. In both cases the first factor has high loadings for Mg, Al, Si, Ca, Ti, Mn and Fe, and represents soil

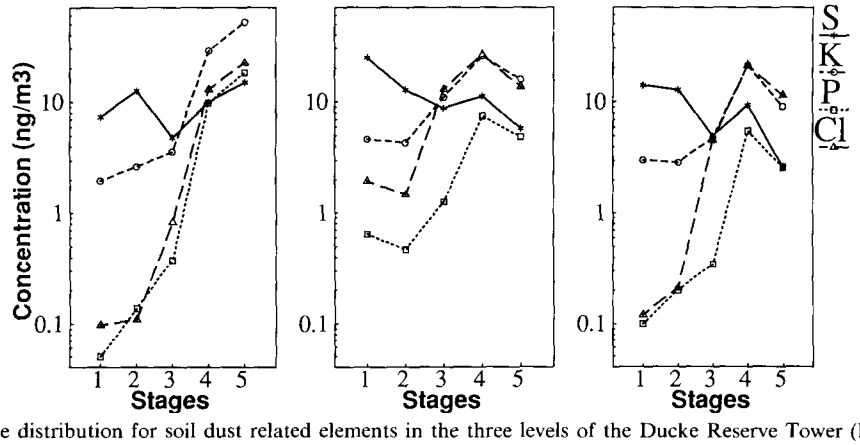

Fig. 2. Elemental size distribution for soil dust related elements in the three levels of the Ducke Reserve Tower (left: ground level, middle: canopy level, right: top level). The 50% cutoff diameters for the cascade impactor stages 1, 2, 3, 4, and 5 are 0.25, 0.5, 1, 2 and 4 μm, respectively.

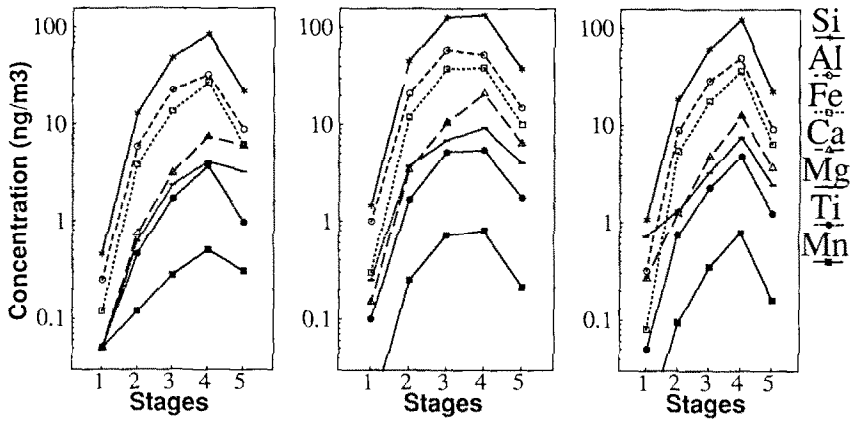

Fig. 3. Elemental size distribution for biogenic related elements at the three levels of the Ducke Reserve Tower (left: ground level, middle: canopy level, right: top level). The 50% cutoff diameters for the cascade impactor stages 1, 2, 3, 4, and 5 are 0.25, 0.5, 1, 2 and 4 μm, respectively.

dust. The second factor has high loadings for P, S, K, and Zn, and represents the biogenic aerosol. The communalities are very high for all variables. The same results were observed at 5 different sites and for both coarse and fine particle fractions collected by stacked filter units in the ABLE-2B experiment [14]. Fig. 1 presents the elemental profiles obtained by the APFA procedure for the soil dust and biogenic factors (concentrations are normalized to the sum of the measured trace elements). For the soil factor, daytime and nighttime samples give almost identical profiles, although the data bases were totally different. The interelement ratios (Ti/Fe, Si/Fe, etc.) agree quite well with those in Mason's average crustal rock composition [35]. For the biogenic component there is a substantial difference between the day and night profiles, with the nighttime profile showing higher concentrations for P, S, K, and Rb. This is probably due to the fact that the boundary layer at nighttime collapses into the forest canopy [36,34], so that the atmospheric dispersion of biogenic aerosols produced under the forest canopy becomes difficult and the boundary layer aerosol thereafter is enriched with biogenic particles.

Aerosol size distributions were measured at the three levels of the Ducke Tower (top level at 45 m high; canopy level at 28 m high, and ground level). Fig. 2 shows the size distributions for the soil-dust related elements for each of the three levels. All size distributions are very similar, and peak at stage 4 (2-4 μm size range). Fig. 3 shows the size distributions for the biogenic related elements. Phosphorus and chlorine are mainly present in the coarse mode at all three levels. Potassium is clearly bimodal, but the coarse mode prevails at all levels, especially at the ground level. There is a pronounced fine mode sulphur component at the canopy and top levels, but this mode is significantly reduced at ground level. This would indicate that the production of fine sulphur particles occurs mainly in the canopy, and above it, in the free troposphere.

5. Conclusions

Through the use of PIXE together with absolute principal factor analysis, it was possible to distinguish a biogenic component in the Amazon Basin aerosol. This component was characterized by the presence of K, P, S, and Zn. Also a soil dust related component was identified, containing Mg, Al, Si, Ca, Ti, Mn and Fe, and exhibiting an elemental profile similar to that of average crustal rock. The cascade impactor data showed that there are large differences in the size distributions of the soil and biogenic related elements, with sulphur and potassium exhibiting a clearly bimodal character. The biogenic aerosol particles are responsible for a significant fraction of the airborne aerosol concentrations. Considering the vast area of tropical rain forests and the concentrations measured in this work, biogenic particles should be very important in the global aerosol budget and in the global biogeochemical cycles of various elements.

We like to thank Alberto Setzer, Tarsis Germano and Marcio Vilella for their help during the sampling program. Thanks are also due to Jost Heintzenberg for supplying the fine particle aerosol sampler, and to Jack Winchester for very useful discussions during the planning of this experiment. W.M. is indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for research support. P.A. acknowledges grant no. 85/3566-3 from the "FAPESP – Fundação de Amparo a Pesquisa do Estado de São Paulo", and grant no. 27.12 from the BID-USP Project.

References

[1] H. Riehl and J.S. Malkus, Geophysica 6 (1958) 503.
[2] R.C. Harriss, S.C. Wofsy, M. Garstang, E.V. Browell, L.C. Mollion, R.J. McNeal, J.M. Hoell, R.J. Bendura, S.M. Beck, R.L. Navarro, J.T. Riley and R.L. Snell, J. Geophys. Res. 93 (1988) 1351.
[3] M. Garstang, J. Scala, S. Greco, R. Harriss, S. Beck, E. Browell, G. Sachse, G. Gregory, G. Hill, J. Simpson, W.K. Tao and A. Torres, J. Geophys. Res. 93 (1988) 1528.
[4] H. Cachier, P. Buat-Menard, M. Fontugne and R. Chesselet, J. Atmos. Chem. 3 (1985) 469.
[5] G. Crozat, J.L. Domergue, J. Baudet and V. Bogui, Atmos. Environ. 12 (1978) 1917.
[6] D.R. Lawson and J.W. Winchester, Geophys. Res. Lett. 5 (1978) 195.
[7] D.R. Lawson and J.W. Winchester, Science 205 (1979) 1267.
[8] C. Orsini, P. Artaxo and M. Tabacnicks, Atmos. Environ. 16 (1982) 2177.
[9] P. Artaxo, Ph.D. Thesis, Instituto de Fisica, Universidade de São Paulo, Brazil (December 1985).
[10] P. Artaxo, C. Orsini, L.C. Bouéres and A. Leslie, Acta Amazônica 12 (1982) 39.
[11] P. Artaxo, C. Orsini, M. Tabacnicks, L.C. Boueres and A. Leslie, Annais Academia Brasileira de Ciencias 54 (1982) 299.
[12] P. Artaxo and C. Orsini, in: Aerosols: Formation and Reactivity, ed. G. Israel (Pergamon Journals, London, 1986) p. 148.
[13] P. Artaxo, H. Storms, F. Bruynseels, R. Van Grieken and W. Maenhaut, J. Geophys. Res. 93 (1988) 1605.
[14] P. Artaxo, W. Maenhaut, H. Storms and R. Van Grieken, submitted to J. Geophys. Res. (1989).
[15] W. Seiler and P.J. Crutzen, Climatic Change 2 (1980) 207.
[16] A.C.D. Leslie, Nucl. Instr. and Meth. 181 (1981) 345.
[17] B.R. Fish, Science 175 (1972) 1239.
[18] G. Crozat, Tellus 31 (1979) 52.
[19] R.C. Schnell and G. Vali, Nature 236 (1973) 163.
[20] W. Beauford, J. Barber and A.R. Barringer, Science 195 (1977) 571.
[21] B.R.T. Simoneit, Marine Chem. 5 (1977) 443.
[22] G.C. Curtin, H.D. King and E.L. Mosier, J. Geochemical Explor. 3 (1974) 245.
[23] P. Artaxo and C. Orsini, Nucl. Instr. and Meth. B22 (1987) 259.
[24] R.C. Harriss, M. Garstang, S.C. Wofsy, S.M. Beck, R.J. Bendura, J.R.B. Coelho, J.W. Drewry, J.M. Hoell, Jr., P.A. Matson, R.J. McNeal, L.C.B. Molion, R.L. Navarro, V. Rabine and R.L. Snell, submitted to J. Geophys. Res. (1989).
[25] S.A.E. Johansson and J.L. Campbell, PIXE – A Novel Technique for Elemental Analysis (Wiley, New York, 1988).
[26] W. Maenhaut, A. Selen, P. Van Espen, R. Van Grieken and J.W. Winchester, Nucl. Instr. and Meth. 181 (1981) 399.
[27] W. Maenhaut, H. Raemdonck and M.O. Andreae, Nucl. Instr. and Meth. B22 (1987) 248.
[28] G.C. Thurston and J.D. Spengler, Atmos. Environ. 19 (1985) 9.
[29] H.H. Harman, Modern Factor Analysis, third ed. revised. (University of Chicago Press, Chicago, 1976).
[30] R.C. Henry, C.W. Lewis, P.K. Hopke and H.J. Williamson, Atmos. Environ. 18 (1984) 1507.
[31] N.Z. Heidam, Atmos. Environ. 16 (1982) 1923.
[32] P.K. Hopke, Receptor Modeling in Environmental Chemistry (Wiley, New York, 1985).
[33] R.W. Talbot, M.O. Andreae, H. Berresheim, P. Artaxo, M. Garstang, R.C. Harriss, K.M. Beecher and S.M. Li, submitted to J. Geophys. Res. (1989).
[34] M. Garstang, et al., submitted to Bull. Am. Meteor. Soc. (1989).
[35] B. Mason, Principles of Geochemistry, 3rd ed. (Wiley, New York, 1966).
[36] S. Greco, R. Swap, M. Garstang, S. Ulanski, M. Shipham, R.C. Harriss, R. Talbot, M.O. Andreae and P. Artaxo, submitted to J. Geophys. Res. (1989).