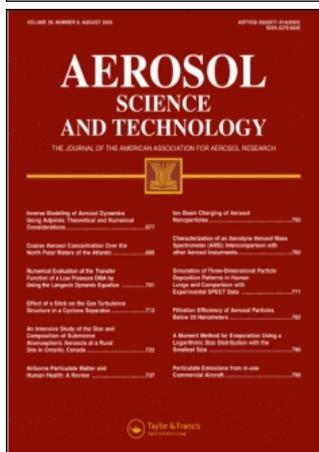


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Aerosol Inorganic Composition at a Tropical Site: Discrepancies Between Filter-Based Sampling and a Semi-Continuous Method

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Aerosol Inorganic Composition at a Tropical Site: Discrepancies Between Filter-Based Sampling and a Semi-Continuous Method

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The concentrations of the water-soluble inorganic aerosol species, ammonium (NH_4^+), nitrate (NO_3^-), chloride (Cl^-), and sulfate (SO_4^{2-}), were measured from September to November 2002 at a pasture site in the Amazon Basin (Rondonia, Brazil) (LBA-SMOCC). Measurements were conducted using a semi-continuous technique (Wet-annular denuder/Steam-Jet Aerosol Collector: WAD/SJAC) and three integrating filter-based methods, namely (1) a denuder-filter pack (DFP: Teflon and impregnated Whatman filters), (2) a stacked-filter unit (SFU: polycarbonate filters), and (3) a High Volume dichotomous sampler (HiVol: quartz fiber filters). Measurements covered the late dry season (biomass burning), a transition period, and the onset of the wet season (clean conditions). Analyses of the particles collected on filters were performed using ion chromatography (IC) and Particle-Induced X-ray Emission spectrometry (PIXE). Season-dependent discrepancies were observed between the WAD/SJAC system and the filter-based samplers. During the dry season, when $\text{PM}_{2.5}$ ($D_p \leq 2.5 \mu\text{m}$) concentrations were $\sim 100 \mu\text{g m}^{-3}$, aerosol NH_4^+ and SO_4^{2-} measured by the filter-based samplers were on average two times higher than those determined by the WAD/SJAC. Concentrations

of aerosol NO_3^- and Cl^- measured with the HiVol during daytime, and with the DFP during day- and nighttime also exceeded those of the WAD/SJAC by a factor of two. In contrast, aerosol NO_3^- and Cl^- measured with the SFU during the dry season were nearly two times lower than those measured by the WAD/SJAC. These differences declined markedly during the transition period and towards the cleaner conditions during the onset of the wet season ($\text{PM}_{2.5} \sim 5 \mu\text{g m}^{-3}$); when filter-based samplers measured on average 40–90% less than the WAD/SJAC. The differences were not due to consistent systematic biases of the analytical techniques, but were apparently a result of prevailing environmental conditions and different sampling procedures. For the transition period and wet season, the significance of our results is reduced by a low number of data points. We argue that the observed differences are mainly attributable to (a) positive and negative filter sampling artifacts, (b) presence of organic compounds and organosulfates on filter substrates, and (c) a SJAC sampling efficiency of less than 100%.

INTRODUCTION

Atmospheric pollution in the Northern Hemisphere is driven by fossil fuel combustion and agricultural practices, often causing aerosol chemical composition to be dominated by ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}), mixed with sea-salt in coastal regions. The aerosol composition in the tropical Amazon Basin is dominated by organic matter, while inorganic aerosol species account for less than 20% of the total aerosol mass (Andreae and Crutzen 1997). Inorganic aerosol compounds like $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 , and NH_4Cl are formed from their gaseous precursors ammonia (NH_3), sulfur dioxide (SO_2), nitric acid (HNO_3), and hydrochloric acid (HCl). Whereas $(\text{NH}_4)_2\text{SO}_4$ is stable and non-volatile, particulate NH_4NO_3 and NH_4Cl form via reversible thermodynamic

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phase equilibria with NH_3 , HNO_3 , and HCl (Mozurkewich 1993; Stelson and Seinfeld 1982). NH_4NO_3 and NH_4Cl are therefore semi-volatile, and their stability strongly depends on ambient temperature (T) and relative humidity (RH) (see, e.g., Pathak and Chan 2005).

In the past, inorganic aerosol constituents have been sampled in the Amazon region using filter-based methods without pre- or post-stages to trap gaseous compounds (e.g., Allen and Miguel 1995; Graham et al. 2003; Mace et al. 2003; Talbot et al. 1988; Yamasoe et al. 2000). Long filter sampling intervals (hours to days) may favor condensation of gaseous compounds (e.g., HNO_3 , NH_3 , SO_2) on substrates (positive sampling artifact) or evaporation of semi-volatile species from substrates (negative sampling artifact), driven mainly by varying environmental conditions (T and RH) and a change of filter loading during the sampling period (e.g., Appel et al. 1984; Fehsenfeld et al. 1990; Lipfert 1994). Moreover, chemical reactions may occur on filter materials, leading to the formation and loss of HNO_3 (Eatough et al. 1995; Slanina et al. 2001). In the last decade, measurement methods that are less prone to artifacts have been developed. They include, for example, filter-pack methods and dry-coated diffusion denuders, but also several continuous sampling devices. Nowadays, the denuder technique allows semi-continuous measurements with high time resolution and high sampling efficiency (Simon and Dasgupta 1993; Slanina et al. 1992). Denuder devices may be combined with recently developed aqueous-phase aerosol collectors (Simon and Dasgupta 1995; Slanina et al. 2001; Weber et al. 2001). Currently, this is the only available approach for collecting gas and aerosol species simultaneously and selectively with high time resolution. The first semi-continuous measurements of aerosol NO_3^- , Cl^- , NH_4^+ , and SO_4^{2-} and their gaseous precursors HNO_3 , HCl , NH_3 , and SO_2 in a tropical environment were made in southwestern Amazonia (Rondônia, Brazil) within the framework of the LBA-SMOCC 2002 campaign (Large Scale Biosphere Atmosphere Experiment in Amazonia, Smoke Aerosols, Clouds, Rainfall and Climate: Aerosols from Biomass Burning Perturb Global and Regional Climate) (Andreae et al. 2004; Trebs et al. 2004). Measurements were conducted using a wet-annular denuder (WAD) in combination with a Steam-Jet Aerosol Collector (SJAC) (Slanina et al. 2001). Various conventional filter-based samplers were deployed simultaneously including a denuder-filter pack (DFP: Teflon and impregnated Whatman filters), a stacked-filter unit (SFU: polycarbonate filters) and a High Volume dichotomous sampler (HiVol: quartz-fiber filters). Gas-to-particle conversion processes and aerosol chemistry at this tropical site have been investigated in previous studies (e.g., Falkovich et al. 2004; Fuzzi et al. 2007; Hoffer et al. 2006; Mayol-Bracero et al. 2002; Trebs et al. 2005).

This article presents an intercomparison of the semi-continuous WAD/SJAC system with three integrating filter-based samplers (DFP, SFU, and HiVol) for the inorganic aerosol species NO_3^- , Cl^- , NH_4^+ , and SO_4^{2-} , performed for the first time under tropical conditions. The intercomparison is made

for three different environmental situations: (a) heavily polluted conditions during the late dry (biomass burning) season (12–23 September 2002, $\text{PM}_{2.5}$ [particulate matter with $D_p \leq 2.5 \mu\text{m}$] $\sim 100 \mu\text{g m}^{-3}$), (b) moderately polluted conditions (transition period, 07–31 October 2002, $\text{PM}_{2.5} \sim 20 \mu\text{g m}^{-3}$), and (c) a period with fairly clean conditions during the onset of the wet season (01–14 November 2002, $\text{PM}_{2.5} \sim 5 \mu\text{g m}^{-3}$). Differences between semi-continuous techniques and filter-based methods had been found to be smaller than 30% at Northern Hemisphere extratropical sites (e.g., Drewnick et al. 2003; Lee et al. 2003; Schaap et al. 2004; Slanina et al. 2001; Weber et al. 2003). This study will show that these findings may not always hold under tropical conditions.

MATERIALS AND METHODS

Field Site

Field measurements were performed at a pasture site in the state of Rondônia, Brazil, located in the southwestern part of the Amazon Basin (Fazenda Nossa Senhora Aparecida, FNS, $10^\circ 45' 44''$ S, $62^\circ 21' 27''$ W, 315 m asl). The vegetation at FNS is dominated by grass, and the site is used as a cattle ranch (~ 200 “Blanco” cattle). High temperatures ($> 35^\circ\text{C}$ during daytime) and high RHs (close to 100% at nighttime), accompanied by large day-night variations are typical for FNS (Trebs et al. 2005). A detailed description of the measurement site is given in Andreae et al. (2002) and Kirkman et al. (2002).

Sampling

Preparation and handling of the filter substrates, as well as the semi-continuous measurements were carried out in an air-conditioned wooden house. The integrating samplers were mounted outside the house within a fenced-off area (for details see Trebs et al. 2006). The filter sampling periods were 12 hours daytime and 12 hours nighttime during the late dry (biomass burning) season, 24 hours during the transition period, and 48 hours during the onset of the wet season. In order to obtain representative samples for day and night during the 24 and 48 hours sampling periods, sampling was performed during 2 or 4 consecutive days or nights, respectively. Table 1 summarizes information about the samplers and analytical methods employed for determining the inorganic aerosol composition, including the institutions operating the samplers and the abbreviations used for them in this article.

Semi-Continuous Measurements (WAD/SJAC)

Air was sampled from 530 cm above ground through a vertical polyethylene conduit with an inner diameter of 7 cm. The air flow in the conduit was generated by a suction fan in the conduit bottom. A sub-sample of the air was aspirated from the center of the conduit's cross section area at a flow rate of $\sim 17 \text{ l min}^{-1}$ (STP: 298.15 K and 1000 hPa) through a steel elbow (Trebs et al. 2004). The sampled air was then drawn through

TABLE 1

Overview of aerosol samplers and analytical techniques employed for the measurement of the aerosol species NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} at FNS during LBA-SMOCC 2002

Abbreviation	Sampler	Sampling height	Institution*	Analyses
WAD/SJAC	Wet-annular denuder/Steam-Jet Aerosol Collector ($\text{PM}_{2.5}$ or TSP)	5.3 m	MPI-C	NH_4^+ (FIA), NO_3^- , Cl^- , and SO_4^{2-} (IC), on-line (Trebs et al. 2004)
DFP	Denuder-filterpack ($\text{PM}_{2.5}$ or TSP)	5.3 m	UPR—ITES, MPI-C	NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} (IC)
SFU	Stacked filter units ($\text{PM}_{2.5}$ and PM_{10})	4 m	USP, WIS, UGent	NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} (IC), elemental S (PIXE)
HiVol	HiVol sampler ($\text{PM}_{2.5}$ only)	1.8 m	UGent, WIS	NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} (IC)

(*) MPI-C: Max Planck Institute for Chemistry (Mainz, Germany).

UPR—ITES: University of Puerto Rico—Institute for Tropical Ecosystem Studies (San Juan, Puerto Rico).

USP: University of São Paulo (Brazil).

WIS: Weizmann Institute of Science (Rehovot, Israel).

UGent: Ghent University (Belgium).

a PFA Teflon tubing connection to the sampling system in an air conditioned laboratory. During the field experiment, the steel elbow was replaced periodically with a pre-impactor ($\text{PM}_{2.5}$ size cut; type 413, University Research Glassware), such that aerosol samples of either $\text{PM}_{2.5}$ or total suspended particulate matter (TSP) were collected in alternating cycles (1–3 days) (Trebs et al. 2004; Trebs et al. 2005). Aerosol particles were collected using a Steam-Jet Aerosol Collector (SJAC) (Khlystov et al. 1995). Gaseous compounds, such as ammonia (NH_3), nitric acid (HNO_3), nitrous acid (HNO_2), hydrochloric acid (HCl), and sulfur dioxide (SO_2) were removed prior to aerosol collection by a horizontally aligned rotating wet-annular denuder (WAD) that was coated with a 10^{-4} M NaHCO_3 absorption solution. Analyses were performed on-line, using ion chromatography (IC) for anions and flow injection analysis (FIA) for ammonium (NH_4^+) (Slanina et al. 1992). The IC was calibrated continuously using an internal bromide standard (Slanina et al. 2001). The reliability of the internal standard was checked periodically by injecting standard solutions of Cl^- , NO_3^- , and SO_4^{2-} . The FIA was calibrated once per week with NH_4^+ standard solutions. Measurement intervals were 20 min (biomass burning season), 40 min (transition period), and 60 min (wet season). Measurement uncertainties were estimated to remain below 15% (Trebs et al. 2004). A detailed description of the WAD/SJAC system and the analytical procedures is given elsewhere (Slanina et al. 1992; Slanina et al. 2001; Trebs et al. 2004).

Denuder-Filterpack (DFP)

The DFP employed in this study (see Table 1) was previously described by Keuken (1989) and Slanina et al. (2001), and

is composed of a stainless steel filter holder and two dry-annular denuders made of borosilicate glass tubes. The two denuders and the filter pack were aligned horizontally in tandem at the outer wall of the wooden house. During sampling, the air entered (a) the first denuder coated with a 0.1 M sodium fluoride solution to scavenge acidic trace gases (HNO_3 , HCl , and SO_2), (b) the second denuder coated with a 0.5 M phosphoric acid (H_3PO_4) solution to trap gaseous NH_3 , (c) a Teflon filter (47 mm, Zeffluor, pore size $2 \mu\text{m}$) to collect aerosol particles, (d) a NaF impregnated Whatman 41 filter paper as backup for evaporated acidic gases, and (e) a H_3PO_4 impregnated Whatman 41 filter as backup for gaseous NH_3 . Air was aspirated in parallel to the WAD/SJAC system from the center of the conduit's cross section area at a flow rate of $\sim 5 \text{ l min}^{-1}$. Thus, the cut-off size for aerosol particles sampled with the DFP was the same as for the WAD/SJAC system. Denuder samples were extracted immediately after sample collection. The denuder extracts and the Whatman/Teflon filter samples were stored in polyethylene vials at 4°C until analysis.

Extraction and analyses of the DFP samples were performed at the Max Planck Institute for Chemistry in Mainz, Germany (MPI-C) (see Table 1). The NaF and H_3PO_4 impregnated Whatman 41 filter papers were extracted in ultra-pure water (UPW). The Teflon filters were wetted with methanol (CH_3OH) overnight and UPW was added the following day. The filter extracts were shaken every 5–10 minutes for one hour. Isocratic separation on ion exchange columns and subsequent suppressed conductivity detection was used for both anion and cation analyses. For the determination of NH_4^+ , an IC separation column (Dionex CS14) preceded by a guard column (Dionex CG14)

was used. Samples were injected manually via a 20 μl loop into a 10 mM methanesulfonic acid (MSA) eluent, containing 5% CH_3OH . The anions Cl^- , NO_3^- , and SO_4^{2-} were determined using an IC separation column (Dionex, AS9-HC, 4 mm) preceded by a guard column (Dionex, AG9). Samples were injected manually via a 50- μl loop into a 7 mM sodium carbonate (Na_2CO_3) eluent. The detection limit (LOD) of the MPI-C ion chromatograph is 0.2 $\mu\text{mol l}^{-1}$ for all ions.

Stacked-Filter Units (SFUs)

SFUs generally select two aerosol size fractions. The SFU sampler employed in this study (see Table 1) was a Gent PM₁₀ SFU (Hopke et al. 1997). The sampler was mounted at a height of 4 m above ground and was equipped with Nuclepore[®] polycarbonate filters (47 mm). The pore sizes of filter stages 1 and 2 were 8 and 0.4 μm , respectively. The filters of stage 1 were Apiezon-coated to minimize particle bouncing. The sampler was operated at a flow rate of $\sim 17 \text{ l min}^{-1}$, resulting in a cut point between the coarse and fine aerosol fraction of $D_p \sim 2.0 \mu\text{m}$. The sum of the two stages provides PM₁₀ ($D_p \leq 10 \mu\text{m}$). Samples were stored at 4°C until analysis. Extraction and analyses of the SFU samples were performed at the Weizmann Institute of Science (WIS) in Rehovot, Israel. Filter samples were extracted in 4 ml of UPW with 15-min vortex agitation. IC analyses were performed using a Varian ProStar HPLC system equipped with a Dionex ED50 electrochemical detector. A Dionex AS11 analytical column preceded by a guard column (Dionex AG11) was employed for anion analysis (gradient elution with NaOH). Cations were analyzed using a Dionex CS12A column and guard column (Dionex CG12A) using an MSA eluent (18 mM). The LOD of the WIS ion chromatograph is 1 $\mu\text{mol l}^{-1}$ for cations and 3 $\mu\text{mol l}^{-1}$ for anions. A detailed description of the analyses is given in Falkovich et al. (2004). Additionally, SFU filter samples were subjected to Particle-Induced X-ray Emission spectrometry (PIXE) (Artaxo and Orsini 1987) at the University of São Paulo, Brazil (USP) and at the Ghent University (UGent) to determine elemental sulfur (S) (“elemental” as used in this article, refers to the result of an elemental analysis, i.e., the unspicated concentration of an element in the sample).

High Volume Dichotomous Filter Sampler (HiVol)

A HiVol sampler that separates fine aerosol particles ($D_p < 2.5 \mu\text{m}$) from the coarse aerosol fraction ($D_p > 2.5 \mu\text{m}$) was also employed (see Table 1) (Solomon et al. 1983). The sampler was mounted at a height of 1.8 m above ground. The flow rates of the sampler were 300 l min^{-1} for the fine fraction and 30 l min^{-1} for the coarse fraction. For both size fractions, the particles were collected with a front/back tandem system of quartz-fiber filters (102 mm diameter, Pallflex[®], Pall Corporation; prebaked for 24 hours at 550°C) (for details see Falkovich et al. [2004]). HiVol filter samples were stored at -25°C . During shipment they were kept frozen (using dry ice or cooling elements). The temperature was then below -5°C until analysis. Extraction was performed

TABLE 2

Filter blanks of the aerosol species NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} expressed as average percentage [%] of typically observed concentrations at FNS during LBA-SMOCC 2002

Blanks	NH_4^+ [%]	NO_3^- [%]	Cl^- [%]	SO_4^{2-} [%]
DFP-Teflon	28	33	8	21
SFU-IC	5	15	35	15
SFU-PIXE	—	—	—	50
HiVol	10	10	—	10

twice in UPW with 15-min vortex agitation. The collected supernatant was centrifuged for 5 min. IC analyses of the HiVol samples were carried out at WIS; the analytical procedures were the same as for the SFU samples.

A number of field blanks were taken by drawing air through the integrating samplers for 10 seconds. These blanks were analyzed in the same way as the air samples and the obtained values were then subtracted from the measured concentrations. Blank values for integrating filter samplers are presented in Table 2.

Although, the accuracy for all analytical procedures applied to DFP, SFU, and HiVol samples was within 10%, the average filter blanks in Table 2 are quite high, which may indicate a variable positive bias of the results.

RESULTS

Results will be presented for (a) dry season (biomass burning), (b) transition period, and (c) onset of the wet season. For the intercomparison, the WAD/SJAC data were averaged over the respective filter collection periods. All concentrations are given at standard conditions of 298.15 K and 1000 hPa. Depending on the inlet used for the WAD/SJAC and the DFP (see above), either the measured SFU fine aerosol (PM_{2.0}) or coarse aerosol (PM₁₀) concentration is considered. For the HiVol sampler only the fine aerosol fraction (PM_{2.5}) was analyzed and will be used for the intercomparison. It is well known that inorganic compounds like $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 , and NH_4Cl mostly reside in the fine aerosol fraction, with the exception of NO_3^- that may be associated to some extent with coarse mode mineral cations. Thus, it is often justifiable to assume that the concentrations of the compounds measured in PM_{2.0} and/or PM_{2.5} and PM₁₀ samples are comparable, i.e., the contribution of particles with $D_p > 2.5 \mu\text{m}$ to the concentration of water-soluble inorganic ions is marginal. This, however, may not hold during aerosol droplet growth periods and under the presence of organic aerosol species during high RH conditions (above 90%).

Concentrations

During the LBA-SMOCC experiment, the contribution of inorganic species to PM_{2.5} remained below 20% during all seasons. PM_{2.5} was $\sim 100 \mu\text{g m}^{-3}$ during the dry season, it decreased to

$20 \mu\text{g m}^{-3}$ during the transition period, and to about $5 \mu\text{g m}^{-3}$ during the wet season (Trebs et al. 2005).

Figure 1 shows box-and-whisker plots of the concentrations observed for daytime (D) and nighttime (N) during the dry (biomass burning) season. Note that for the DFP only concentrations determined on the Teflon filters are presented. Results from the impregnated Whatman backup filters are not included because they are biased by very high blank values as well as by high (non-volatile) SO_4^{2-} concentrations (see below).

Measured aerosol NH_4^+ concentrations ranged from ~ 250 to $\sim 3500 \text{ ng m}^{-3}$ (Figure 1a). The overall range of daytime aerosol NH_4^+ concentrations measured with WAD/SJAC, DFP and SFU agreed moderately well, while daytime aerosol NH_4^+ determined with the HiVol sampler was at least two times higher. Median nighttime aerosol NH_4^+ values measured with integrating filter samplers were at least a factor of two higher than those observed with the WAD/SJAC system.

In the case of aerosol NO_3^- , observed concentrations during the dry season ranged from ~ 100 to $\sim 6500 \text{ ng m}^{-3}$ (Figure 1b). Aerosol NO_3^- results for the DFP exceed those from the WAD/SJAC by at least a factor of three during day- and nighttime. Aerosol NO_3^- collected with the HiVol during daytime was also about two times higher than that measured with the WAD/SJAC. By contrast, aerosol NO_3^- determined with the SFU during day- and nighttime, and with the HiVol during nighttime was nearly two times lower than measured with the WAD/SJAC.

Aerosol Cl^- concentrations were, on average, one order of magnitude lower than concentrations of the other ions and behaved similarly to aerosol NO_3^- (Figure 1c). While reasonable agreement between WAD/SJAC and DFP was found, aerosol Cl^- concentrations observed with the SFU during day- and nighttime and with the HiVol during nighttime were about a factor of two lower than those measured with the WAD/SJAC. In contrast, aerosol Cl^- collected with the HiVol during daytime was almost two times higher than the values derived with the WAD/SJAC.

The aerosol SO_4^{2-} concentrations observed at FNS during the dry season ranged from ~ 500 to $\sim 6000 \text{ ng m}^{-3}$ (Figure 1d). The lowest concentrations and variabilities were found for the WAD/SJAC and DFP samples. Except for DFP daytime samples, median concentrations found with integrating filter-based samplers were at least two times higher than those measured with the WAD/SJAC. While aerosol SO_4^{2-} measured with the WAD/SJAC sampler was comparable for day and night, results from integrating filter samplers show differences between day- and nighttime. Elemental S from SFU filters that were subjected to PIXE is presented in Figure 1d, after converting the measured S concentration to SO_4^{2-} . These median aerosol SO_4^{2-} values are approximately 20% higher than aerosol SO_4^{2-} collected on the SFU filters analyzed with IC, and agree relatively well with aerosol SO_4^{2-} determined with the HiVol. Daytime levels of SFU-PIXE and SFU-IC SO_4^{2-} are in better agreement compared to the daytime aerosol SO_4^{2-} measured with the HiVol. For nighttime samples the agreement is better between SFU-PIXE and HiVol.

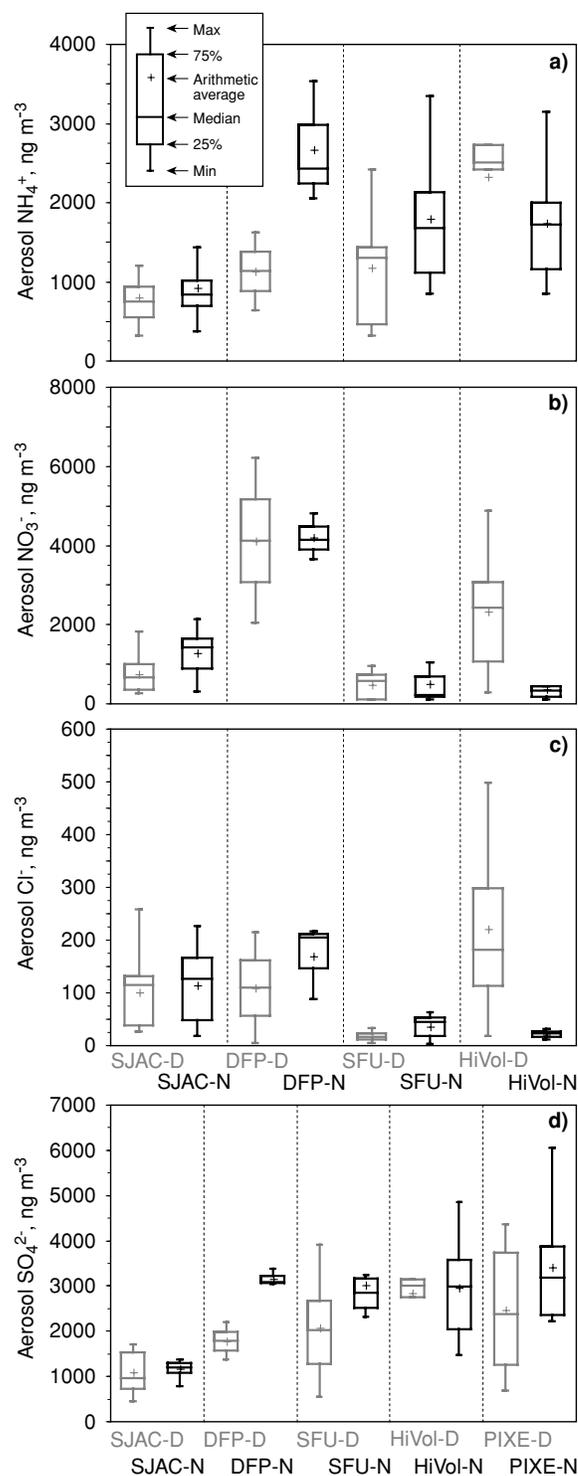


FIG. 1. Box-and-whisker plots showing statistical distributions of concentrations during daytime (D) and nighttime (N) for aerosol ions (a) NH_4^+ , (b) NO_3^- , (c) Cl^- , and (d) SO_4^{2-} measured with the WAD/SJAC, DFP (Teflon filters), SFU (polycarbonate filters), and HiVol sampler (quartz-fiber filters) during the dry (biomass burning) season (12–23 Sep.) at FNS during LBA-SMOCC 2002 (HiVol samples were analyzed for $\text{PM}_{2.5}$ only, elemental S is presented as SO_4^{2-} equivalent assuming that the measured S concentration is entirely attributable to aerosol SO_4^{2-}).

Separate day- and nighttime results from the transition period and the onset of the wet season are not presented, because sampling periods extended over 24 or 48 hours to collect sufficient material on the filter substrates for chemical analyses. Due to occasional WAD/SJAC instrument problems and air concentrations below the LOD of the analytical methods, the data availability during these two periods is low. Measured concentrations are summarized in Table 3.

During the transition period, pollution from biomass burning decreased and aerosol concentrations of all ionic species dropped by almost one order of magnitude. The agreement between aerosol NH_4^+ and SO_4^{2-} median concentrations measured by WAD/SJAC, DFP and SFU increased considerably, while concentrations measured with the HiVol were still at least two times higher than concentrations measured with the WAD/SJAC (Table 3). PIXE results for aerosol SO_4^{2-} still exceed IC results from the SFU by $\sim 15\%$. Fair agreement was found among all samplers for aerosol Cl^- and NO_3^- concentrations, which were already very low during the transition period (medians $< 50 \text{ ng m}^{-3}$ and $< 250 \text{ ng m}^{-3}$, respectively; Table 3).

During the onset of the wet season, when conditions were fairly clean, the median concentrations of all inorganic ions decreased to below 420 ng m^{-3} . Concentrations measured with the WAD/SJAC exceeded those of filter-based samplers significantly (Table 3). The DFP results are lower than those of the WAD/SJAC system indicating perhaps a loss of particles in the denuder sample train during very high RHs. PIXE results for aerosol SO_4^{2-} agree very well with IC results.

As depicted in Figure 1 and Table 3, remarkable differences exist also among the integrating samplers. Concentrations measured with the SFU sampler equipped with polycarbonate filters are generally lower than those measured with the HiVol sampler that was operated with quartz-fiber filters. Results from the DFP and the HiVol sampler show differences of a factor two or three. It should be kept in mind that results shown for the DFP only represent concentrations found on the Teflon filters (cf. Figure 1 and Table 3). Evaporative losses determined on the backup filters were up to 50% of the values found on the Teflon filters and would thus further increase the total concentration found with the DFP.

The differences between the WAD/SJAC and the filter-based samplers show a clear seasonal trend that is reflected in Figure 2.

For aerosol NH_4^+ and SO_4^{2-} the average difference declines from 80–140% during the dry season to 15–55% during the transition period, and turns negative to about –40% during the onset of the wet season. In the case of aerosol NO_3^- and Cl^- , the differences exhibit a large variability during the dry season, being mainly positive (15–75%) during daytime and negative (50%) during nighttime. The relative differences change sign and all become negative during the transition period (–50––75%) and the wet season (–90%). Generally, results from integrating filter-based samplers exceed those of the WAD/SJAC during the dry season, but filter samplers yielded comparable or even lower

concentrations than the WAD/SJAC towards cleaner conditions during the onset of the wet season (Figure 2).

Correlations

The squared correlation coefficient r^2 describes the proportion of variance in common between two variables, i.e., the larger the r^2 is; the more X and Y are dependent on each other. Since measurement errors occur in both X and Y directions, the conventional (Y on X) ordinary least squares regression is not suitable for this study. Ayers (2001) recommended using the reduced major axis analysis (RMA) regression (also called geometric mean regression [Halfon 1995]) for the comparison of air quality data. This method minimizes the product of the X and Y deviations between the data values and the fitted values. Linear RMA correlations of the results obtained with the WAD/SJAC and the filter-based samplers (DFP, SFU, and HiVol) are presented in Table 4(a,b).

For dry season samples, correlations were generally better during nighttime than during daytime. Reasonable correlations were found between WAD/SJAC and DFP for aerosol NH_4^+ , NO_3^- , and Cl^- ($r^2 = 0.62, 0.88, \text{ and } 0.85$), which are characterized by slopes of 1.5, 1.2, and 0.9, but had relatively large intercepts (Table 4a). Although acceptable correlations ($r^2 > 0.5$) were observed for the daytime dry season samples between WAD/SJAC and HiVol for aerosol NO_3^- and SO_4^{2-} , the slopes were larger than two. Rather poor correlations ($r^2 < 0.5$) were identified for nighttime dry season samples between WAD/SJAC, SFU, and HiVol for aerosol NH_4^+ and SO_4^{2-} , with slopes higher than two and large intercepts. Between the filter-based samplers, SFU and HiVol, good correlations were identified for all nighttime samples, except for aerosol Cl^- , which correlated better during daytime. However, except for aerosol NH_4^+ , the RMA regression between SFU and HiVol resulted in slopes significantly smaller or higher than unity and/or large intercepts. Not surprisingly, the correlations for aerosol SO_4^{2-} from the SFU sampler determined with IC and PIXE were very good during day- and nighttime with $r^2 > 0.9$. Slopes higher than unity indicate that some S was associated with compounds other than SO_4^{2-} . All other correlations for dry season samples were very poor with $r^2 < 0.2$ and large standard errors of slopes and/or intercepts.

For the transition period, reasonable r^2 values were calculated for aerosol NH_4^+ between WAD/SJAC and HiVol, for aerosol NO_3^- between WAD/SJAC and DFP, and for aerosol SO_4^{2-} between all samplers (Table 4b). Except for aerosol NO_3^- and Cl^- , the slopes are in most cases larger than unity. Considering the absolute concentration measured during the transition period (Table 3), very large intercepts (positive and negative) were obtained. Correlations improved during the transition period in comparison to the dry season.

A good correlation was found during the onset of the wet season for aerosol NH_4^+ between WAD/SJAC and SFU ($r^2 = 0.89$), but the slope was significantly smaller than unity (Table 4b).

TABLE 3

Summary of results (median, 25th percentile and 75th percentile of all samples) for aerosol ions NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} measured with the WAD/SJAC, DFP, SFU and HiVol sampler during the transition period (07–31 Oct) and the onset of the wet season (01–14 Nov) at FNS during LBA-SMOCC 2002

Season	Sampler	NH_4^+ (ng m^{-3})			NO_3^- (ng m^{-3})			Cl^- (ng m^{-3})			SO_4^{2-} (ng m^{-3})			$\text{S}^{(3)}$ (PIXE) (ng m^{-3})		
		m	P 0.25	P 0.75	m	P 0.25	P 0.75	m	P 0.25	P 0.75	m	P 0.25	P 0.75	m	P 0.25	P 0.75
Transition period	WAD/SJAC	409.3	242.1	553.0	217.4	174.7	340.5	33.9	27.7	46.3	457.3	366.4	596.4	—	—	—
	DFP ⁽¹⁾	247.3	144.5	411.6	166.0	130.0	327.3	13.7	7.9	20.9	647.2	603.7	866.4	—	—	—
	SFU	470.6	136.2	796.2	187.6	105.2	314.1	20.5	13.7	25.8	889.5	371.6	1572.4	1036.6	329.9	1835.4
Wet season	HiVol ⁽²⁾	854.3	817.0	888.0	182.1	71.0	525.6	15.4	12.9	17.5	1383.4	1376.1	1444.8	—	—	—
	WAD/SJAC	340.3	259.8	367.9	135.4	120.3	165.0	48.6	27.8	57.8	411.0	282.2	551.8	—	—	—
	DFP	30.5	18.5	59.9	<LOD	<LOD	<LOD	25.7	13.9	124.2	136.3	118.9	138.0	—	—	—
	SFU	189.7	166.1	219.3	60.4	9.4	67.2	7.4	4.2	9.8	349.6	311.3	372.5	349.9	333.9	395.4
	HiVol	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

⁽¹⁾only concentrations determined on the Teflon filters are presented.

⁽²⁾HiVol samples were analyzed for $\text{PM}_{2.5}$ only (coarse fraction of TSP samples is not included).

⁽³⁾elemental S is presented as the SO_4^{2-} equivalent by assuming that the measured S concentration is entirely attributable to aerosol SO_4^{2-} .

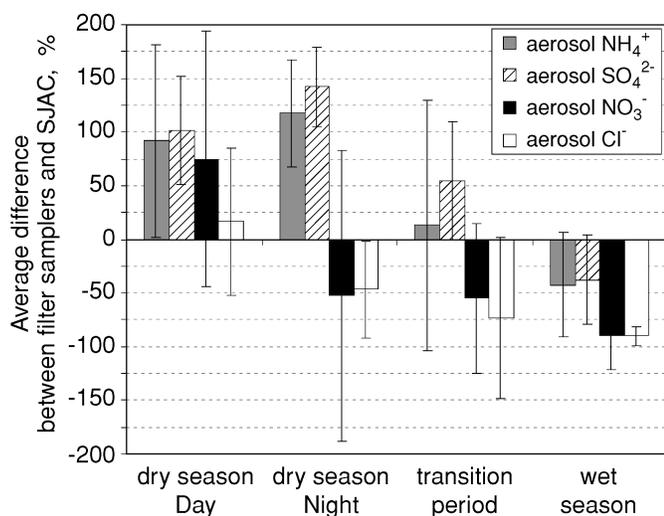


FIG. 2. Average relative differences (assuming the WAD/SJAC is the reference) between the mean of concentrations determined from integrating samplers (DFP, SFU, and HiVol) and concentrations measured with the WAD/SJAC for the dry season (day- and nighttime), transition period and wet season at FNS during LBA-SMOCC 2002. Error bars indicate standard deviations of differences.

Reasonable correlation was again found for aerosol SO₄²⁻ from the SFU sampler determined with IC and PIXE ($r^2 = 0.64$). All other correlations for wet season samples were poor with $r^2 < 0.2$.

In most cases, poor correlation coefficients and/or slopes significantly higher/lower than unity or large intercepts were obtained between WAD/SJAC and filter-based methods. The calculated slopes and intercepts do not reveal a systematic or seasonal dependence. The limited data set during cleaner periods could bias our statistical results.

DISCUSSION

Influence of Meteorology and Chemistry

To our knowledge, all intercomparison studies of this nature have been performed in the extratropical Northern Hemisphere. While other studies found significant differences for individual data points and/or special sampling conditions, we could not identify any reference that consistently shows large discrepancies between semi-continuous methods and filter-based samplers for inorganic aerosol species. The differences found in our study are largest during the dry season (biomass burning) and decline towards cleaner conditions during the onset of the wet season (Figure 2), suggesting that the observed differences are related to biomass burning activity or environmental parameters such as T and RH. The following evaluations will focus on the dry (biomass burning) season, when the best data availability was achieved, highest concentrations were observed, and largest discrepancies between samplers were found. Such an evaluation would be difficult for the transition period and wet season since the meteorology varied significantly during the filter sampling

intervals of 24 or 48 hours. During the dry season, average nighttime RHs at our tropical site were higher than 90% and daytime RHs ranged from 50 to 60%. Average temperatures ranged from 20 to 25°C during nighttime and mostly exceeded 30°C during daytime (Trebs et al. 2005).

The aerosol chemical composition and behavior in the Amazon Basin differs remarkably from the extratropical Northern Hemisphere. At the FNS site, thermodynamic equilibrium permitted the formation of aqueous NH₄NO₃ and NH₄Cl only during nighttime (RH > 90%), and mineral cations (especially K⁺) significantly balanced fine mode aerosol NO₃⁻ and SO₄²⁻ during daytime (Trebs et al. 2005). Due to molar ratios of NH₃/SO₂ higher than 10 at the FNS site, aerosol (NH₄)₂SO₄ was a minor component of the inorganic aerosol fraction, and gaseous NH₃ was largely neutralized by low-molecular weight (LMW) polar organic acids (Trebs et al. 2005). A similar aerosol composition was observed, for example, by Yu et al. (2006).

Aerosol NH₄⁺ and SO₄²⁻

Figure 3 shows the relative difference (%) between SFU and WAD/SJAC for aerosol NH₄⁺ and SO₄²⁻, measured during the dry (biomass burning) season, along with RH.

The differences between SFU and WAD/SJAC follow a comparable variation for aerosol NH₄⁺ and SO₄²⁻ and were always higher during nighttime (RH > 90%) than during daytime (RH < 70%). During the period presented in Figure 3, gas-phase concentrations measured with the WAD/SJAC were on average 2000 ng m⁻³ for NH₃ and 800 ng m⁻³ for SO₂ and were typically lower during nighttime than during daytime. This indicates that the differences of aerosol NH₄⁺ and SO₄²⁻ between SFU and WAD/SJAC are not directly related to the abundance of their gaseous precursors. Generally, large discrepancies between the semi-continuous method and integrating samplers are

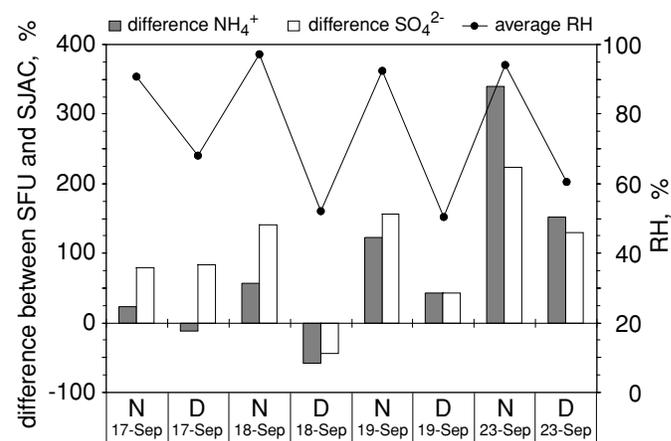


FIG. 3. Relative difference (%) (assuming the WAD/SJAC is the reference) between the concentrations of aerosol NH₄⁺ and SO₄²⁻ measured with SFU (polycarbonate filters) and WAD/SJAC for four days (D) and nights (N) during the dry (biomass burning) season (left Y-axis) along with the measured relative humidity (RH) (averages for respective sampling interval, right Y-axis) at FNS during LBA-SMOCC 2002.

TABLE 4

Correlation coefficients (r^2) and reduced major axis analysis (RMA) regression results ($Y = (A \pm \sigma_A) + (B \pm \sigma_B) * X$, where σ_A and σ_B are the standard errors of intercept A and slope B, respectively) for WAD/SJAC, DFP, SFU, and HiVol samplers.

Correlations for the DFP sampler refer only to concentrations determined on the Teflon filters. Results are shown for (a) the late dry (biomass burning) season (day- and nighttime listed separately); (b) the transition period and the onset of the wet season (clean conditions) at FNS during LBA-SMOCC 2002 (fields were left empty if values were smaller than the limit of detection or $N < 3$)

(a)									
		Dry season-DAY				Dry season-NIGHT			
Combination X – Y	Compound	r^2	$A \pm \sigma_A$ [ng m ⁻³]	$B \pm \sigma_B$ [1]	N	r^2	$A \pm \sigma_A$ [ng m ⁻³]	$B \pm \sigma_B$ [1]	N
WAD/SJAC-DFP	Aerosol NH ₄ ⁺	—	—	—	—	0.62	986 ± 659	1.5 ± 0.5	3
WAD/SJAC-SFU		0.25	-549 ± 743	1.9 ± 0.7	5	0.01	-490 ± 972	2.6 ± 1.0	6
WAD/SJAC-HiVol		0.30	403 ± 800	2.1 ± 0.8	5	0.01	-326 ± 879	2.3 ± 0.9	6
SFU-HiVol		0.10	375 ± 911	1.7 ± 0.7	5	0.99	118.9 ± 79	0.9 ± 0.04	6
WAD/SJAC-DFP	Aerosol NO ₃ ⁻	—	—	—	—	0.88	2044 ± 433	1.2 ± 0.2	3
WAD/SJAC-SFU		0.33	-126 ± 257	0.6 ± 0.2	5	0.01	-897 ± 564	1.2 ± 0.4	7
WAD/SJAC-HiVol		0.01	-501 ± 1489	3.0 ± 1.4	5	0.01	-839 ± 312	0.6 ± 0.2	6
SFU-HiVol		0.35	96 ± 1035	4.8 ± 1.7	5	0.88	152 ± 50	0.5 ± 0.07	6
WAD/SJAC-DFP	Aerosol Cl ⁻	—	—	—	—	0.85	33 ± 34	0.9 ± 0.2	3
WAD/SJAC-SFU		0.40	-3 ± 9	0.2 ± 0.1	4	0.69	-0.2 ± 11	0.5 ± 0.1	5
WAD/SJAC-HiVol		0.77	-147 ± 88	3.6 ± 0.8	5	0.34	7 ± 5	0.1 ± 0.04	6
SFU-HiVol		0.58	-65 ± 117	18 ± 5.9	4	0.01	9 ± 5	0.2 ± 0.1	4
WAD/SJAC-DFP	Aerosol SO ₄ ²⁻	—	—	—	—	0.03	433 ± 1554	2.1 ± 1.2	3
WAD/SJAC-SFU		0.40	-989 ± 870	2.9 ± 0.7	5	0.23	-110 ± 1146	2.6 ± 0.9	6
WAD/SJAC-HiVol		0.50	171 ± 910	2.2 ± 0.7	5	0.34	2163 ± 1752	4.2 ± 1.4	6
SFU-HiVol		0.01	1125 ± 887	0.83 ± 0.36	5	0.91	-1981 ± 608	1.6 ± 0.2	6
SFU(IC)-SFU(PIXE)		0.95	-46 ± 292	1.2 ± 0.12	5	0.98	-1992 ± 309	1.9 ± 0.1	6
(b)									
		Transition period				Wet season			
Combination X – Y	Compound	r^2	$A \pm \sigma_A$ [ng m ⁻³]	$B \pm \sigma_B$ [1]	N	r^2	$A \pm \sigma_A$ [ng m ⁻³]	$B \pm \sigma_B$ [1]	N
WAD/SJAC-DFP	Aerosol NH ₄ ⁺	0.18	-145 ± 150	1.1 ± 0.4	7	0.01	-373 ± 258	1.3 ± 0.7	3
WAD/SJAC-SFU		0.19	-449 ± 353	2.1 ± 0.8	6	0.89	169 ± 10	0.18 ± 0.1	3
WAD/SJAC-HiVol		0.68	10 ± 196	1.7 ± 0.4	5	—	—	—	—
SFU-HiVol		0.13	426 ± 196	0.8 ± 0.4	—	—	—	—	—
WAD/SJAC-DFP	Aerosol NO ₃ ⁻	0.96	-356 ± 62	1.5 ± 0.1	5	—	—	—	—
WAD/SJAC-SFU		0.01	-91 ± 123	0.9 ± 0.4	6	0.02	-27 ± 81	1.0 ± 0.6	3
WAD/SJAC-HiVol		0.50	-209 ± 170	1.5 ± 0.5	5	—	—	—	—
SFU-HiVol		0.55	11 ± 99	1.4 ± 0.5	4	—	—	—	—
WAD/SJAC-DFP	Aerosol Cl ⁻	0.72	-16 ± 9	0.8 ± 0.2	4	—	—	—	—
WAD/SJAC-SFU		0.60	-11 ± 11	0.7 ± 0.3	4	0.04	4.6 ± 2.5	0.03 ± 0.02	3
WAD/SJAC-HiVol		0.29	1.8 ± 2.1	0.3 ± 0.1	4	—	—	—	—
SFU-HiVol		—	—	—	—	—	—	—	—
WAD/SJAC-DFP	Aerosol SO ₄ ²⁻	0.47	-127 ± 235	1.6 ± 0.4	8	0.17	104 ± 14	0.06 ± 0.03	—
WAD/SJAC-SFU		0.65	-679 ± 445	2.6 ± 0.6	6	0.11	165 ± 98	0.5 ± 0.2	4
WAD/SJAC - HiVol		0.98	-119 ± 110	2.4 ± 0.9	5	—	—	—	—
SFU-HiVol		0.63	653 ± 322	0.9 ± 0.9	4	—	—	—	—
SFU(IC)-SFU(PIXE)		0.98	871 ± 59	1.1 ± 0.1	7	0.64	54 ± 71	0.9 ± 0.2	7

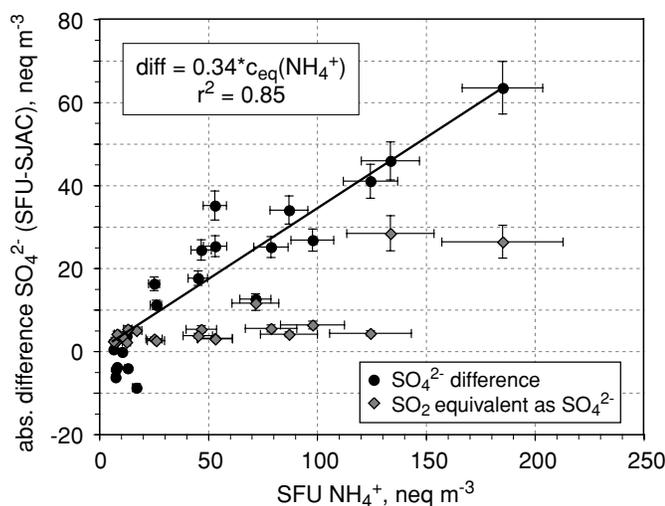


FIG. 4. Absolute aerosol SO_4^{2-} difference between SFU (IC) and WAD/SJAC versus aerosol NH_4^+ measured with the SFU sampler at FNS during LBA-SMOCC 2002. SO_2 measured with the WAD is plotted as aerosol SO_4^{2-} equivalent possibly formed on the filter. Linear regression was done with data from all seasons ($N = 20$). Error bars indicate measurement uncertainty.

unexpected, since $(\text{NH}_4)_2\text{SO}_4$ is a stable compound. Potential chemical interference due to Apiezon on the SFU filters can be excluded because sulfur was also measured by PIXE from samples collected with an SDI impactor (cf. Fuzzi et al. 2007). Sulfur values from Apiezon-coated SFU filters and impactor filters agreed within 10%. However, the presence of alkaline species may provoke adsorption of SO_2 on filter substrates and subsequent oxidation with ozone (O_3) and/or hydrogen peroxide (H_2O_2) (Appel et al. 1984; Coutant 1977; Eatough et al. 1995). High RHs could promote trapping of small droplets on the filter substrates leading to retention of gaseous species. Since NH_3 was present in excess to neutralize acidic species (Trebs et al. 2005), one possible explanation for the discrepancies could be the adsorption of NH_3 and subsequent retention and oxidation of SO_2 on filter materials during nighttime, when RH exceeded 90%. In order to investigate this further, a linear correlation of the absolute aerosol SO_4^{2-} difference between SFU and WAD/SJAC versus aerosol NH_4^+ measured with the SFU sampler is shown in Figure 4.

A clear relationship between these two quantities is visible, i.e., the higher the amount of aerosol NH_4^+ collected on the SFU, the larger is the difference of SO_4^{2-} between SFU and WAD/SJAC. In some cases, the amount of SO_2 appeared to be sufficient to produce the observed SO_4^{2-} discrepancy (Figure 4). Nevertheless, in order to fully explain the differences, Figure 4 suggests that more SO_2 than measured by the WAD would have to have been adsorbed by the filter.

The relative differences between the concentrations of aerosol NH_4^+ and SO_4^{2-} measured with the HiVol, DFP, and WAD/SJAC during the same days as shown in Figure 3 were mostly positive (not shown), i.e., concentrations measured with

the HiVol and DFP exceeded those of the WAD/SJAC (cf. Figure 1). No distinct dependence on daytime or nighttime as in the case of the SFU was visible. However, the difference between DFP and WAD/SJAC for aerosol SO_4^{2-} was smaller than 20% for three daytime samples during the dry season, suggesting that the retention of SO_2 by the dry-coated diffusion denuders may increase the comparability between WAD/SJAC and filter-based methods.

In comparison, during the Atlanta Supersite Experiment in 1999, integrating filter-based samplers were compared amongst themselves and agreed on average within $\pm 10\%$ for aerosol NH_4^+ and SO_4^{2-} (Solomon et al. 2003). A comparison between semi-continuous and filter aerosol SO_4^{2-} measurements in Atlanta revealed differences of up to 80% for individual days (Weber et al. 2003). However, on average the relative difference between integrating filter-based samplers and semi-continuous instruments in Atlanta was $\leq 25\%$. During a study in New York City, filters measured up to 28% more aerosol SO_4^{2-} than on-line instruments like the Particle-Into-Liquid Sampler (PILS) and Aerosol Mass Spectrometer (AMS) (Hogrefe et al. 2004). Good agreement of the PILS instrument with a filter-based sampler was reported from aircraft measurements in the western Pacific (TRACE-P and ACE Asia) (Ma et al. 2004). From a study in tropical Hong Kong, negligible positive SO_4^{2-} artifacts of 2% and 7% for, e.g., Teflon filters were reported (Pathak and Chan 2005). At a subtropical urban site in Taiwan, small positive aerosol SO_4^{2-} artifacts ranging from 8 to 15% and some negative NH_4^+ artifacts ranging from -17 to -21% were found on quartz-fiber filters (Tsai and Perng 1998). Very good comparability was achieved between WAD/SJAC and DFP for aerosol NH_4^+ and SO_4^{2-} in the Netherlands (Slanina et al. 2001).

An important difference of our study to those mentioned above is the presence of biomass burning aerosols containing large quantities of organic compounds (e.g., humic-like substances) (Hoffer et al. 2006). If water-soluble organic compounds are retained by filter substrates, they interact with inorganic compounds sampled on the filter, particularly during very humid conditions at nighttime (RH > 90%) (e.g., $\text{NH}_3 + \text{R-COOH} \rightarrow \text{R-COO}^- + \text{NH}_4^+$ (Trebs et al. 2005)). Moreover, our somewhat higher PIXE results (Figure 1, Table 3) suggest that some S was also attributable to other compounds, possibly organosulfates (Blando et al. 1998; Liggio and Li 2006; Romero and Oehme 2005). These organosulfates (also called sulfate esters) can form from reactions of acidic aerosol SO_4^{2-} with carbonyls in the atmosphere (Iinuma et al. 2007; Surratt et al. 2007). It has been suggested that conventional inorganic SO_4^{2-} chemical analysis may underestimate the total SO_4^{2-} mass in ambient aerosols (Liggio and Li 2006). In our case, this argument is not supported, since the analytical IC procedures were similar for filter-based methods and WAD/SJAC. However, the main difference is that in the WAD/SJAC ionic species were extracted within a few seconds after sample collection, while filters were transported and stored for several weeks before extraction and analysis. If organosulfates had (at least partially) caused

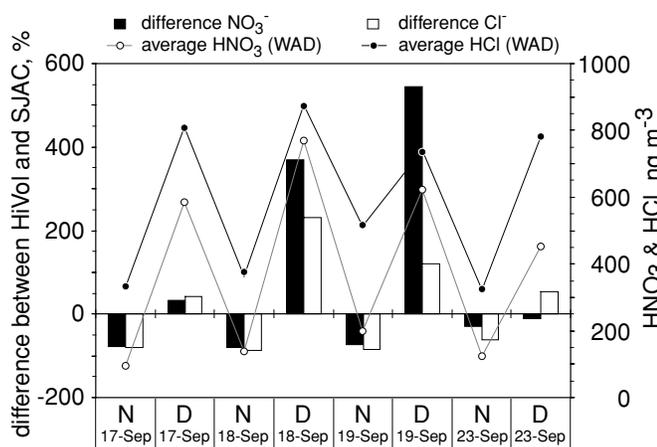


FIG. 5. Relative difference (%) (assuming the WAD/SJAC is the reference) between the concentrations of aerosol NO_3^- and Cl^- measured with HiVol (quartz-fiber filters) and WAD/SJAC for four days (D) and nights (N) during the dry season (left Y-axis) along with gas phase concentrations (HNO_3 and HCl) (averages of respective sampling interval; measured with WAD; (right Y-axis) at FNS during LBA-SMOCC 2002.

the observed differences during the dry (biomass burning) season; this implies that they decomposed into SO_4^{2-} during storage and/or extraction of filters such that more SO_4^{2-} was detected by IC on filter samples.

Aerosol NO_3^- and Cl^-

Figure 5 shows the relative difference (%) between aerosol NO_3^- and Cl^- measured with HiVol and WAD/SJAC during the dry (biomass burning) season along with HNO_3 and HCl.

The relative difference (%) between HiVol and WAD/SJAC for aerosol NO_3^- and Cl^- and is negative during nighttime (HiVol concentrations are lower than those of the WAD/SJAC) and positive during the day (HiVol concentrations exceed those of the WAD/SJAC). Aerosol NO_3^- and Cl^- are regarded as volatile aerosol compounds. Most studies report increasing evaporation (negative artifact) of volatile species from quartz-fiber filters with increasing temperature (Fehsenfeld et al. 1990; Keck and Wittmaack 2005; Schaap et al. 2004). The high equilibrium pressure of the salts at elevated temperatures give rise to high rates of volatilization in flowing air (Wittmaack and Keck 2004). However, our results show the opposite: more NO_3^- and Cl^- was found during daytime ($T > 30\%$) on HiVol samples than measured with the WAD/SJAC (positive artifact). As reflected in Figure 5, the relative differences are apparently related to the concentrations of HNO_3 and HCl, which exceeded 500 ng m^{-3} during the day and were below 500 ng m^{-3} during the night. This implies that the measured NO_3^- and Cl^- masses on the quartz-fiber filters were dependent on the abundance of gaseous precursors HNO_3 and HCl. Aerosol NO_3^- can also be lost from filter substrates due to chemical interaction between nitrate salts, particulate H_2SO_4 , and gaseous HCl (Appel and Tokiwa 1981; Tsai and Perng 1998), which may have been the case at FNS under humid nighttime conditions. The relative difference between

the concentrations of aerosol NO_3^- and Cl^- measured with SFU (polycarbonate filters) and WAD/SJAC were mostly negative (not shown), i.e., the SFU sampler recovered less aerosol NO_3^- and Cl^- than the WAD/SJAC (cf. Figure 1). The differences do not show a consistent day/night variation and no dependence on gas-phase precursors HNO_3 and HCl is observed. Underestimation of the aerosol NO_3^- concentration is well known for Teflon filters (Appel et al. 1979; Fehsenfeld et al. 1990; Neil 2006; Schaap et al. 2004) and may also apply to Nuclepore[®] polycarbonate filters at the FNS site. Moreover, each sampler had different filter face velocities, which could impact the collection of semi-volatile material, e.g., a higher face velocity could potentially lead to larger evaporative losses. Thus, NO_3^- and Cl^- loss from the SFU could be caused by the large pressure drop (0.5 bar) across the $0.4 \mu\text{m}$ polycarbonate filter. This pressure drop was only around 0.28 bar across the HiVol quartz-fiber filter.

The relative difference between the concentrations of aerosol NO_3^- and Cl^- measured with DFP (Teflon filters) and WAD/SJAC (not shown, see also Figure 1) was always positive and no consistent variations were found between day and night. The concentrations found on the impregnated Whatman backup filters (not shown, see above) were often up to 50% of the values found on the Teflon filters. Previous studies in the Netherlands report that the DFP may suffer from artifact evaporation of NH_4NO_3 from the Teflon filter (Slanina et al. 2001). Additionally, NH_4NO_3 particles can be collected by the dry annular denuders (Khlystov et al. 1995). In our case, however, the concentrations of aerosol species measured with the DFP are significantly higher than measured with the WAD/SJAC, especially when biomass burning was prevalent. It should be noted that even under these polluted conditions, the concentrations of inorganic compounds at FNS are at least a factor of two lower than in the Netherlands. As shown in Figure 1, the concentrations of aerosol NH_4^+ and NO_3^- determined with the DFP also significantly exceeded those determined with the SFU and HiVol during the dry season. Moreover, total concentrations for all ions determined with the DFP (i.e., sum of denuder, Teflon filter, and Whatman backup filter) exceeded the total concentrations measured with the WAD/SJAC system (sum of gas and aerosol phase) by a factor of three to four (not shown). Theoretically, evaporation and condensation artifacts should not introduce significant biases to DFP results. However, in order to obtain reliable results using the DFP, a special laboratory should be used, where no other, possibly interfering activities are allowed (Slanina et al. 2001). As indicated by very high blank values as well as by high SO_4^{2-} concentrations found on the impregnated Whatman backup filters, these requirements were presumably not met under the prevailing field conditions at the FNS site. This assumption is supported by large intercepts found for WAD/SJAC-DPF correlations, in particular for aerosol NO_3^- (see Table 4).

In comparison, a comprehensive set of integrating samplers, including filters and combinations of coated denuders and filters were intercompared during the Atlanta Supersite Experiment in 1999 (Solomon et al. 2003). In contrast to our study, most of

these samplers agreed on average within $\pm 30 - 35\%$ for aerosol NO_3^- at concentrations comparable to those observed during the dry season at the FNS site. Good agreement was found for aerosol NO_3^- measured with filter samplers, a PILS and an AMS in New York City (Hogrefe et al. 2004). A reasonable overall comparability between semi-continuous and integrating samplers was also observed for aerosol NO_3^- during several other studies in the United States (e.g., Weber et al., 2003; Wittig et al. 2004; Rattigan et al. 2006). However, on individual days Weber et al. (2003) observed differences of a factor of two to three between semi-continuous and integrating samplers. Results from Pittsburgh (Wittig et al. 2004) and New York (Rattigan et al. 2006) showed differences of a factor of two or more between R&P semi-continuous aerosol NO_3^- and 24-h integrated measurements for individual days. Significant differences (average of 50%) for aerosol NO_3^- were also observed between the R&P semi-continuous and Nylon filters (after removal of ambient gases using a MgO denuder) in Baltimore (Harrison et al. 2004). A study in tropical Hong Kong reported aerosol NO_3^- losses of 36 to 55% and significant evaporation of HCl causing a chloride loss of 61 to 68% from Teflon filters (Pathak and Chan 2005). Negative NO_3^- artifacts ranging from -16 to -21% and large negative Cl^- artifacts due to volatilization of NH_4Cl , ranging from -24 to -54% on quartz-fiber filters were found at a subtropical urban site in Taiwan (Tsai and Huang 1995).

Potential Inlet Problems and SJAC Sampling Efficiency

The WAD/SJAC system was compared in Atlanta to other semi-continuous devices for aerosol SO_4^{2-} and NO_3^- and the agreement was within 10–15% (Weber et al. 2003). An inter-comparison of the WAD/SJAC system with different filter-based methods in eastern Germany showed maximal differences of 18% for aerosol SO_4^{2-} and NO_3^- (Schaap et al. 2004). During other studies, online-instruments recovered about 85% of the aerosol SO_4^{2-} mass collected by the filter techniques (Drewnick et al. 2003). It was argued that deviations can be the result of a combination of positive sampling artifacts on the filters with negative biases of the semi-continuous measurements (inlet line losses, limited collection efficiency for small particles).

In our study at a tropical site, consistent qualitative and quantitative differences between WAD/SJAC and integrating samplers were observed. The regression parameters in Table 4 neither exhibit a systematic structure nor a distinct seasonal variation. Large intercepts may allude to blank problems, but consistent systematic deviations were not observed. Hence, we exclude the possibility that these differences are due to the different analytical procedures used to analyze the samples. However, we like to note that each sampler uses a different method for determining the $\text{PM}_{2.5}$ size selection, which introduces an additional uncertainty (particularly in case of the SFU sampler that only collected $\text{PM}_{2.0}$). We may also not rule out the possibility that the WAD/SJAC method is prone to sampling losses, which may have caused the observed discrepancies to some extent. These include: (a) inlet losses due to non-isokinetic sampling,

(b) collection of particles by the WAD, (c) evaporative losses of NH_4NO_3 particles in the WAD, and (d) insufficient collection of small particles by the SJAC.

Average aerosol losses due to superisokinetic sampling have been estimated to below 3% ($D_p \leq 2.5 \mu\text{m}$) (Trebs et al. 2004). Consequently, possible inlet losses are not considered to contribute significantly to the observed differences. The flow in the WAD is laminar and particle losses may arise either from diffusion or from gravitational settling, which may become relevant for particles with $D_p < 10 \text{ nm}$ and/or $D_p > 1 \mu\text{m}$, respectively (Slanina et al. 1992). Chang et al. (2002) reported that evaporative losses of NH_4NO_3 particles due to disequilibrium after the gases have been removed from the air sample are important for ambient temperatures $> 25^\circ\text{C}$ and for HNO_3 concentrations below $0.1 \mu\text{g m}^{-3}$. They predicted the evaporative loss as a function of residence time in the WAD for a $\text{PM}_{2.5}\text{-NO}_3^-$ fraction of 8%. Considering that the residence time of the air in the WAD for our study was 0.2 seconds, this theoretical prediction results in $\sim 5\%$ evaporative losses of NH_4NO_3 in the WAD. Significant aerosol losses would be observed as elevated concentrations in the WAD (e.g., atypical HNO_3 diel cycles), which were not found during the field measurements (cf. Trebs et al. 2005).

It has been stated previously that the SJAC sampler collects more than 99% of the total aerosol number in the size range of $D_p = 19 - 886 \text{ nm}$ (Khlystov et al. 1995), where most of the discussed inorganic species reside. However, the SJAC sampler was never tested for particles with $D_p < 19 \text{ nm}$, which could contribute to losses. For instance, the first version of the PILS sampler was shown to have collection efficiencies below 80% for particles with $D_p < 100 \text{ nm}$ due to nonactivation of smaller nuclei caused by limited mixing of water vapor and sample air (Weber et al. 2001). Such features may be important also for the SJAC; however, the sampler is normally operated with a laboratory-tested optimum steam injection rate, at which the supersaturation at instantaneous mixing is maximal (Khlystov et al. 1995). It should be considered that the supersaturation in the SJAC at air temperatures of 20°C is about two times higher than at 30°C . This is known to be problematic only when the steam injection rate is too low, but might have contributed to the observed differences, because the temperature of the sample air mostly exceeded 20°C at FNS.

Furthermore, Trebs et al. (2005) reported that K_2SO_4 contributed to the inorganic aerosol fraction. This compound has a deliquescence RH of $\sim 98\%$ and its solubility is at least four times lower than that of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . Figure 6 shows a very good linear correlation ($r^2 = 0.91$) between the observed SO_4^{2-} difference of SFU and SJAC and the measured potassium (K) concentration using PIXE, clearly indicating that the aerosol SO_4^{2-} discrepancy is related to the presence of pyrogenic (K^+ containing) aerosols.

It could be speculated that the time to completely dissolve K_2SO_4 in the SJAC (a few seconds) may have been too short, such that a fraction of SO_4^{2-} was not detected by the IC. In contrast, filters from integrating samplers were shaken or subjected

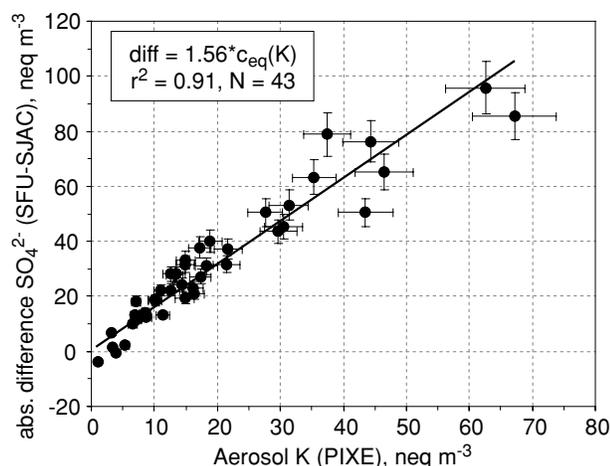


FIG. 6. Absolute aerosol SO_4^{2-} difference between SFU (PIXE) and SJAC versus aerosol K measured by PIXE at FNS during LBA-SMOCC 2002. Error bars indicate measurement uncertainty.

to vortex-agitation for 10 to 15 minutes. However, Figure 6 shows that the amount of equivalent moles of K^+ was not sufficient to entirely cause the observed SO_4^{2-} discrepancy. At least half of the difference was due to other processes, potentially organosulfates and/or suppressed SO_4^{2-} detection due to the presence of organic compounds in the WAD/SJAC system.

CONCLUSIONS

To our knowledge, this article presents the first intercomparison of a semi-continuous method (wet-annular denuder in combination with a Steam-Jet Aerosol Collector (WAD/SJAC)) with state of the art filter-based samplers for inorganic aerosol species (NO_3^- , Cl^- , NH_4^+ , and SO_4^{2-}) under tropical conditions in the Southern Hemisphere (Amazon Basin, Brazil). Measurements were performed during (a) heavily polluted conditions during the late dry (biomass burning) season, (b) moderately polluted conditions (transition period), and (c) a period with fairly clean conditions during the onset of the wet season in 2002.

The agreement between the different sampling methods was poor. During the dry season, a High-Volume dichotomous sampler (HiVol, quartz-fiber filters) and a denuder-filter pack (DFP, Teflon and impregnated Whatman filters) measured concentrations that were on average a factor of two higher than those determined with the WAD/SJAC for all aerosol species. Aerosol NH_4^+ and SO_4^{2-} collected with stacked-filter units (SFU, polycarbonate filters) during the dry season also exceeded those measured with the WAD/SJAC on average by a factor of two, while aerosol concentrations of NO_3^- and Cl^- collected with the SFU were nearly a factor of two lower than those measured with the WAD/SJAC. Differences were most pronounced during the dry season when biomass burning took place and decreased until the onset of the wet season. During cleaner conditions, aerosol

concentrations measured with the WAD/SJAC mostly exceeded those of filter-based methods by about 40–90%. Moreover, substantial positive and/or negative deviations were found amongst the filter-based samplers.

Although, significant differences had been found for individual days during previous intercomparison studies in subtropical and temperate latitudes, on average discrepancies between integrating filter-based samplers and semi-continuous techniques did not exceed $\pm 30\%$. In most of the cases reasonable linear correlations were found for different sampling techniques. In contrast, at our tropical pasture site in the southwestern part of the Amazon Basin, we found consistent differences between filter-based samplers and the semi-continuous method, particularly under polluted conditions (biomass burning). It was not possible to clearly identify the reasons for the observed discrepancies. Most of the linear correlations between the different samplers were unsatisfying and did not reveal systematic differences between analytical techniques. We suggest that the discrepancies were largely attributable to a complex combination of different effects, such as:

- significant changes of environmental conditions (temperature and RH) during long filter sampling periods (positive and negative filter sampling artifacts).
- change of filter loading and filter chemistry during long filter sampling periods, especially under polluted conditions.
- preponderance of the organic aerosol fraction (interaction of inorganic aerosol species with water-soluble organics collected on filter substrates especially under humid nighttime conditions ($\text{RH} > 90\%$)).
- presence of organosulfates that may have decomposed to SO_4^{2-} during filter storage and/or extraction.
- inappropriate laboratory conditions for the handling of (impregnated) denuder-filter pack samples.
- SJAC sampling efficiency less than 100%, potentially affected by pyrogenic aerosol compounds.

We conclude that the measurement of inorganic aerosol compounds is much more challenging under tropical conditions than in the temperate latitudes of the Northern Hemisphere. It is likely that the errors identified in this study also apply to previously published measurements, and that literature data collected under similar conditions should be viewed with caution. Filter sampling artifacts are more significant in tropical regions, where high temperatures and high RHs prevail. We would like to stress that a transfer of methodologies, tested under specific environmental conditions, to other conditions, may cause complex difficulties. The most disconcerting result of our study is that there was no technique that could be identified as a clearly superior “reference” method. This implies that there is a great need for carefully designed studies of the analytical chemistry of the major inorganic species in air masses influenced by biomass burning.

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