

## Corrigendum to: “Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin” published in Atmos. Chem. Phys., 4, 967–987, 2004

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### 3.3 Sampling and analysis

A detailed description of the WAD/SJAC and the analytical procedures is given elsewhere (Slanina et al., 2001; Wyers et al., 1993). A simplified sketch of the sampling system is shown in Fig. 2. The air flow through the instrument ( $\sim 171 \text{ min}^{-1}$ , STP) was generated by a scroll pump outside the wooden house and could be adjusted with a needle valve. The flow was measured continuously (1 min time resolution) with a mass flow meter (Bronkhorst, F-112AC-HA-55-V). After the sample air passed the steel elbow and/or pre-impactor and the PFA Teflon tubing, it entered a horizontally aligned WAD that scavenges soluble gaseous species. Trace gases (such as  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$ ,  $\text{HCl}$  and  $\text{SO}_2$ ) were collected in a  $10^{-4} \text{ M}$   $\text{NaHCO}_3$  absorption solution. The liquid input was controlled automatically by an infrared sensor and a switching valve and the liquid was continuously pumped out of the denuder at a flow rate of  $0.5\text{--}0.6 \text{ ml min}^{-1}$  by a peristaltic pump. The liquid effluent was collected in a sample reservoir (“gas sample”, see Fig. 2). Artifacts due to evaporation of aerosol phase species in the WAD can be excluded because the characteristic time for formation/evaporation of  $\text{NH}_4\text{NO}_3$  is  $>10 \text{ s}$  (Dlugi, 1993), while the mean residence time of the sample air in the WAD is  $\sim 0.002 \text{ s}$  (annulus volume:  $0.0018 \text{ l}$ , flow rate:  $\sim 171 \text{ min}^{-1}$ ).

After the WAD, the air entered a reservoir where it was mixed with steam of highly purified water. The supersaturation causes aerosol particles to grow rapidly (within  $0.1 \text{ s}$ ) into droplets of at least  $2 \mu\text{m}$  diameter. These droplets, containing the dissolved aerosol species were then collected in a cyclone (Khlystov et al., 1995). The cyclone effluent (“aerosol sample”) was transferred into the sample reservoir by a peristaltic pump at a flow rate of  $0.5\text{--}0.6 \text{ ml min}^{-1}$ .

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Collection of liquid samples in the sample reservoir and the following analytical cycles were performed successively for gas and aerosol sample. On-line analyses were carried out using a mobile IC with suppressed conductivity detection. The system was operated with an HPLC separation column (Dionex, IonPac AS12A, 4 mm) preceded by a guard column (Dionex, IonPac AG12A,  $4 \times 50 \text{ mm}$ ). Samples were injected via a  $199 \mu\text{l}$  loop into  $2.7 \text{ mM}$   $\text{Na}_2\text{CO}_3\text{--}0.3 \text{ mM}$   $\text{NaHCO}_3$  eluent. Internal  $\text{Br}^-$  standard addition using a peristaltic pump was performed continuously to calibrate the IC. The conductivity cell of the IC was temperature-stabilized at  $30^\circ\text{C}$  and therefore conductivity measurements were independent from room temperature.

Ammonium ( $\text{NH}_4^+$ ) was determined by FIA (Wyers et al., 1993). The general principle is the addition of  $\text{OH}^-$  ions, converting  $\text{NH}_4^+$  to  $\text{NH}_3$ , which will then pass through a Teflon membrane and is taken up by highly purified water. Subsequent  $\text{NH}_4^+$ -detection is based on conductometry. The conductivity cell of the FIA was not temperature controlled; therefore, conductivity measurements were dependent on temperature. Despite operating an air conditioner, diel temperature variations from  $22^\circ\text{C}$  at night to  $30^\circ\text{C}$  at daytime were observed in the laboratory. Fluctuations of the conductivity due to temperature changes in the air conditioned laboratory were corrected using:

$$\text{Condcorr} = \text{Cond} \times e^{(0.024 \times (20 - T))} \quad (4)$$

where *Condcorr* denotes the corrected conductivity value (mV), *Cond* is the original measured conductivity (mV) and *T* is the observed temperature ( $^\circ\text{C}$ ) in the laboratory. The FIA was calibrated once every week using standard solutions of 50 ppb and 250 ppb  $\text{NH}_4^+$ .

IC and FIA analyses were performed simultaneously for each sample. The analytical sample cycle was purged with ambient air after every run to avoid memory effects of the previous sample solution. The sampling system is fully automated and its software controls the sequence of sample

**Table 2.** Standard deviations  $\sigma_x$  contributing to the total measurement uncertainty  $\sigma_m$ . (index  $x$  is the mixing ratio of the compounds found in aerosol or gas sample ( $m_{\text{liq}}$ ), the mixing ratio of the  $\text{Br}^-$  standard solution ( $m_{\text{Br}(\text{std})}$ ), the liquid flow through the system ( $Q_{\text{liq}}$ ), the analyzed  $\text{Br}^-$  mixing ratio ( $m_{\text{Br}}$ ) or the air mass flow through the system ( $Q_{\text{air}}$ )).

Standard deviations $\sigma_x$	Value/Range	Source/Determination	Mean contribution to $\sigma_m$
<u>IC analyses</u>			
$\sigma_{m_{\text{liq}}}$	0.002–6.8 ppb	5% of $m_{\text{liq}}$ , analysis of standard solutions	18%
$\sigma_{m_{\text{Br}(\text{std})}}$	20 ppb	2% of $m_{\text{Br}(\text{std})}$ , estimated uncertainty of weighting procedures for creating $\text{Br}^-$ standard solutions	2%
$\sigma_{Q_{\text{liq}}}$	0.058 ml min <sup>-1</sup>	10% of $Q_{\text{liq}}$ , standard deviation of mean $Q_{\text{liq}}$ for the entire experiment	57%
$\sigma_{m_{\text{Br}}}$	2.9–12.0 ppb	5% of $m_{\text{Br}}$ , analysis of standard solutions	17%
<u>FIA</u>			
$\sigma_{m_{\text{liq}}}$ (gas)	0.07–25.0 ppb	10% of $m_{\text{liq}}$ , analysis of standard solutions	84%
$\sigma_{Q_{\text{liq}}}$ (gas)	0.017 ml min <sup>-1</sup>	3% of $Q_{\text{liq}}$ , standard deviation of mean $Q_{\text{liq}}$ for the entire experiment	10%
$\sigma_{m_{\text{liq}}}$ (aerosol)	0.15–7.9 ppb	10% of $m_{\text{liq}}$ , analysis of standard solutions	57%
$\sigma_{Q_{\text{liq}}}$ (aerosol)	0.041 ml min <sup>-1</sup>	8% of $Q_{\text{liq}}$ , standard deviation of mean $Q_{\text{liq}}$ for the entire experiment	37%
$\sigma_{Q_{\text{air}}}$	0.02–10.61 min <sup>-1</sup>	Standard deviation of mean $Q_{\text{air}}$ for each sampling interval	6%

injections and integrates detected peak areas. Cycle times for the successive analysis of aerosol and gas sample were set to 20 min (biomass burning season), 40 min (transition period) and 60 min (wet season).

Ambient mixing ratios for gas and aerosol species after IC analyses were determined using the following equation:

$$m = \frac{m_{\text{liq}} \times m_{\text{Br}(\text{std})} \times Q_{\text{liq}} \times G \times M_{\text{air}}}{m_{\text{Br}} \times Q_{\text{air}} \times M_i} \quad (5)$$

where  $m$  is the ambient mixing ratio (ppb),  $m_{\text{liq}}$  is the mixing ratio of the compounds found in aerosol or gas sample (ppb),  $m_{\text{Br}(\text{std})}$  is the mixing ratio of the  $\text{Br}^-$  standard solution (ppb),  $Q_{\text{liq}}$  is the liquid flow through the system (sum of sample and  $\text{Br}^-$  standard flow) (kg s<sup>-1</sup>),  $G$  is the factor to convert the molar weight of ionic compounds analyzed into the molecular weight of the corresponding trace gas (the factor is 1 for aerosol species).  $M_{\text{air}}$  is the molar mass of air (28.96 kg kmol<sup>-1</sup>),  $m_{\text{Br}}$  is the analyzed  $\text{Br}^-$  mixing ratio (ppb),  $Q_{\text{air}}$  is the air mass flow through the system (kg s<sup>-1</sup>) and  $M_i$  is the molar weight of compound  $i$  (kg kmol<sup>-1</sup>). This equation is also valid for calculating ambient mixing ratios of  $\text{NH}_3$  and aerosol  $\text{NH}_4^+$ , excluding the addition of the  $\text{Br}^-$  standard solution to the sample flow.

## 4 Results and discussion

The sampling period was chosen from 12 September to 14 November 2002, covering extensive biomass burning activ-

ity during the dry season (12 to 23 September), an intermediate phase (transition period, 7 to 31 October) and clean conditions during the wet season (1 to 14 November). Due to an instrument failure no samples were collected from 24 September to 7 October.

All results of our measurements of gas and aerosol species are presented as mixing ratios (ppb). All quantities were calculated for standard conditions of 298.15 K, 1000 hPa and dry air, following the recommendations from Schwartz and Warneck (1995) and Mills et al. (1993).

### 4.1 Estimation of measurement uncertainty

The uncertainty of the measurements was estimated applying ‘‘Gaussian Error Propagation’’ to the relationship (5) which resulted in the following formula:

$$\sigma_m = m \times \sqrt{\left(\frac{\sigma_{m_{\text{liq}}}}{m_{\text{liq}}}\right)^2 + \left(\frac{\sigma_{m_{\text{Br}(\text{std})}}}{m_{\text{Br}(\text{std})}}\right)^2 + \left(\frac{\sigma_{Q_{\text{liq}}}}{Q_{\text{liq}}}\right)^2 + \left(\frac{\sigma_{m_{\text{Br}}}}{m_{\text{Br}}}\right)^2 + \left(\frac{\sigma_{Q_{\text{air}}}}{Q_{\text{air}}}\right)^2} \quad (6)$$

where  $\sigma_m$  is the estimated relative uncertainty of the ambient mixing ratio (ppb) and  $\sigma_x$  are the standard deviations of the corresponding parameters (see Eq. 5). Equation (6) was also used to estimate uncertainties for ambient mixing ratios of  $\text{NH}_3$  and aerosol  $\text{NH}_4^+$ , excluding the error associated with the addition of the  $\text{Br}^-$  standard solution to the liquid sample

flow. Calculated total uncertainties  $\sigma_m$  for all measurements and compounds usually ranged from 10–15%, indicating a reliable and stable performance of the instrument. The standard deviations  $\sigma_x$  contributing to the total measurement uncertainty  $\sigma_m$  including their sources are listed in Table 2. For IC analyses, the contribution of  $\sigma_{Q_{liq}}$  was highest (57% of the total error, see Table 2) indicating that the application of peristaltic pumps for the transport of liquid solutions (Br<sup>-</sup> standard and/or sample) is the largest source of measurement error. For FIA analyses, the value of  $\sigma_{m_{liq}}$  had the highest contribution to  $\sigma_m$  (84% and 57% for NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> analyses, respectively). Reasons for that may be an incomplete removal of the temperature dependence by Eq. (4), and also the temperature influence on the equilibrium constant of NH<sub>4</sub>OH and the permeation of NH<sub>3</sub> through the membrane.

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