A FIRST STEP TOWARDS DIRECT MEASUREMENT OF VERTICAL FLUXES OF ATMOSPHERIC PARTICULATE COMPOUNDS

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INTRODUCTION

Recently, much effort has been spent on the determination of vertical particle number fluxes through eddy covariance measurements. However, the chemical composition of the transferred particles has not been considered. A combination of disjunct eddy sampling (Lenschow et al., 1994) and single particle analysis through time-of-flight mass spectrometry (TOF-MS) bears the potential to analyze fluxes of individual particulate compounds.

Fig. 1

SITE & INSTRUMENTS

In May 2002, a YOUNG 81000 sonic anemometer and the time-of-flight mass spectrometer LAMPAS 2 were operated in combination at the forest ecosystem research site "Waldstein" of the Bayreuth Institute of Terrestrial Ecosystem Research (BITÖK) in the "Fichtelgebirge" mountain range, NE-Bavaria, Germany (Fig. 1). The individual particles were introduced into the TOF-MS through stainless steel tubing ending next to the measuring region of the sonic anemometer.

OBJECTIVE

We present the combination of disjunct eddy sampling and TOF-MS single particle analysis and apply a statistical procedure to obtain the turbulent flux direction of an individual particulate compound such as nitrate.

CONCEPT

Irregular disjunct eddy sampling (IDES):

• Correlation between individual TOF-MS analyses and vertical wind velocity

• Analysis statistics may be irregular, because timing of disjunct sampling is driven by the statistics with which particles are hit, ionized and analyzed

• Weighted separation (WS) into virtual reservoirs of updraft (VUR) and downdraft (VDR) particles based on the magnitude of the vertical wind component (Fig. 2)
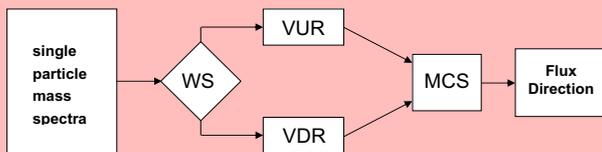
Fig. 2

Virtual accumulation:

• Ambient compound concentration c from characteristic normalized peak area npa and constant relative sensitivity factor RSF:

$$<c> = <npa \cdot RSF> = <npa> \cdot RSF \qquad [Eq.\ 1]$$

• Vertical wind velocity w weighting routine:

$$<w \cdot c> = <w \cdot npa \cdot RSF> = <w \cdot npa> \cdot RSF \qquad [Eq.\ 2]$$

• True eddy accumulation equation adapted for IDES:

$$F_c = <w^+ \cdot npa_{up}> \cdot RSF + <w^- \cdot npa_{down}> \cdot RSF \qquad [Eq.\ 3]$$

• <npa>-scaled transfer velocity v_t:

$$v_t = F_c \cdot RSF^{-1} = <w^+ \cdot npa_{up}> + <w^- \cdot npa_{down}> \qquad [Eq.\ 4]$$

Flux direction:

• The flux direction results from a comparison of the weighted normalized peak areas $<w^+ \cdot npa_{up}>$ and $<w^- \cdot npa_{down}>$ (Eq. 4) representing weighted relative compound concentrations in the virtual updraft and downdraft reservoirs.

• Monte-Carlo type simulations (MCS) (Held et al., 2002) yield a statistical interpretation of the weighted normalized peak area of the VUR and VDR:

• For any given subsample size and confidence level, the maximum deviation from the "true" value can be obtained from a universal confidence matrix for a chemical compound (Fig. 3).

• For VUR and VDR, respectively, the maximum deviation increases with increasing confidence level, yielding confidence intervals within which the "true" concentration lies with a certain confidence (Fig. 4).

• As long as the confidence intervals do not overlap, the flux direction (i.e., the sign of v_t) can be determined with a certain confidence.

APPLICATION

Nitrate flux:

• To study particulate nitrate flux, we applied averaging and normalizing on two characteristic peaks in the negative spectra at the mass-charge ratios (m/z) 46 (NO_2^-) and 62 (NO_3^-).

• From MCS, we obtain a universal confidence matrix for nitrate (Fig. 3). For example, if we analyze 300 particles we expect a deviation between 5% and 10% with a confidence of 75 % (blue dot), while the deviation might be as large as 15% to 20 % with a confidence of 95% (red dot).
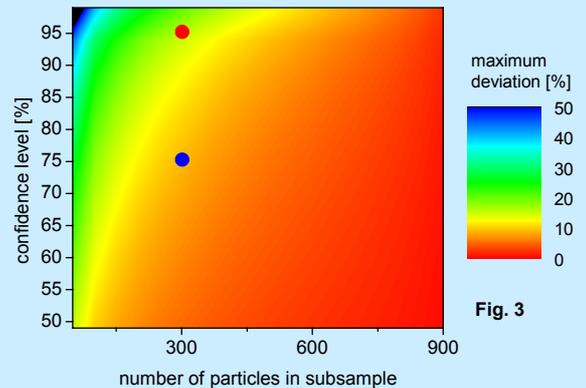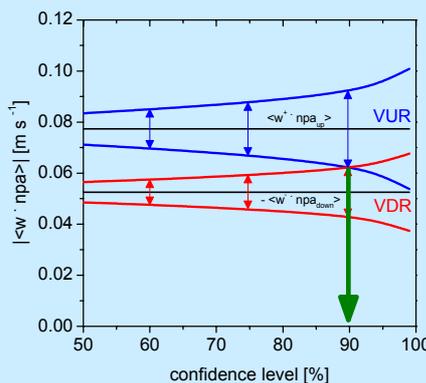
Fig. 3

• On May 25, 2002, we analyzed 172 particles in the VUR and 186 particles in the VDR, yielding weighted relative nitrate concentrations of 0.0773 in the VUR and 0.0525 in the VDR, respectively.

• The corresponding transfer velocity is positive, indicating nitrate emission.

• Acc. Fig. 4, this statement can be trusted with a confidence of 89% (intercept point (green) of VUR (blue) and VDR (red) confidence intervals).

Fig. 4

CONCLUSIONS

• Quasi-instantaneous analysis of individual particles through TOF-MS allows correlation of particulate chemical composition and vertical wind component.

• Individual particle mass spectra are separated into virtual updraft (VUR) and virtual downdraft reservoirs (VDR) in a reversible post-processing routine.

• Averaging of mass spectra information yields a statistical interpretation of the chemical composition of the particle population.

• Comparison of this statistical interpretation allows the determination of flux directions of individual particulate compounds.

REFERENCES
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