GEOPHYSICAL RESEARCH LETTERS, VOL. 30, NO. 19, 2016, doi:10.1029/2003GL017854, 2003

Towards direct measurement of turbulent vertical fluxes of compounds in atmospheric aerosol particles

A. Held,[1,3] K.-P. Hinz,[2] A. Trimborn,[2] B. Spengler,[2] and O. Klemm[1,3]

Received 29 May 2003; revised 22 July 2003; accepted 19 August 2003; published 15 October 2003.

[1] Vertical fluxes of gaseous and particulate compounds in the planetary boundary layer are mainly established through turbulence. To date, it is a challenge to measure vertical fluxes of particles and, even more, the fluxes of compounds in particulates. The combination of disjunct eddy sampling and time-of-flight MS single particle analysis bears the potential to directly measure the turbulent particle flux together with the chemical particle composition. Several obstacles must be overcome before this goal may be achieved. In this paper, we present a statistical procedure, using Monte-Carlo-type simulations, to obtain the flux direction of particulate compounds such as nitrate. A first experimental application of this method yielded emission of particulate NO_3^- from a forest ecosystem on a summer day with a statistical confidence of 89%.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 3379 Meteorology and Atmospheric Dynamics: Turbulence; 3394 Meteorology and Atmospheric Dynamics: Instruments and techniques. **Citation:** Held, A., K.-P. Hinz, A. Trimborn, B. Spengler, and O. Klemm, Towards direct measurement of turbulent vertical fluxes of compounds in atmospheric aerosol particles, *Geophys. Res. Lett.*, *30*(19), 2016, doi:10.1029/2003GL017854, 2003.

1. Introduction

[2] When studying the state and development of ecosystems, it is essential to quantify their nutrient and pollutant exchange with the atmosphere. While turbulent vertical fluxes of several trace gases such as CO_2 are routinely measured, the direct measurement of vertical particle fluxes is still a complex task. Much effort has been spent on measuring vertical particle "number fluxes" over heterogeneous surfaces such as forests [*Gallagher et al.*, 1997; *Buzorius et al.*, 1998, 2000] and urban areas [*Dorsey et al.*, 2002]. "Disjunct eddy sampling methods" [*Rinne et al.*, 2000] were introduced to relax demands on the time response of chemical analysis systems. Ambient air samples are drawn into reservoirs within a short time step on the order of 1/10 s. The sample is then analyzed during a time period of several seconds (e.g., 10 s). Meanwhile, another grab sample is taken into a second reservoir for subsequent analysis. Each (disjunct) sample is attributed to a vertical wind vector component measured with high time resolution as in conventional eddy covariance systems. Although there are significantly less samples than in conventional eddy covariance systems, studies showed that the increase of uncertainty of the flux measurement is small if the time interval between samples is not too long [*Lenschow et al.*, 1994].

[3] The chemical composition of ambient single aerosol particles may be analyzed virtually instantaneously using laser desorption ionization time-of-flight mass spectrometry (LDI-TOF-MS). Several instruments were successfully applied in field campaigns to determine single particle mass spectra online [*Wexler and Prather*, 2000]. Unfortunately, LDI techniques yield only semi-quantitative analysis of single particles due to instrument-specific analytical and inter-particle variability [*Mansoori et al.*, 1994]. Therefore, a direct quantitative flux determination is not possible by use of eddy covariance or disjunct eddy covariance.

[4] Our approach, which is presented in this article for the first time, is to combine TOF-MS with eddy covariance, in analogy to disjunct eddy covariance. In contrast to disjunct eddy sampling, the correlation between individual chemical analyses and the wind vector is computed in a post-processing routine. The timing of MS analysis is driven exclusively by the statistics with which particles are hit, ionized and analyzed. The mass spectra are later correlated with the respective vertical wind vector component, yielding a data set similar to disjunct eddy sampling. However, the time spans between individual analyses may vary. We would therefore call this approach "irregular disjunct eddy sampling" (IDES). A second feature of our approach is the application of a statistical tool to quantify the confidence level of the flux direction of particulate compounds despite the semi-quantitative nature of the chemical analysis. We consider this experiment to be a first step towards direct measurement of turbulent vertical fluxes of compounds in atmospheric particles.

2. Site and Methods

[5] In May 2002, a field experiment was conducted to measure "PArticles and NItrogen above a Coniferous forest" (PANIC, 2002) at the "Waldstein" research site of the Bayreuth Institute of Terrestrial Ecosystem Research (BITÖK) in the "Fichtelgebirge" mountains (NE-Bavaria, Germany). The forest site (776 m asl) - dominated by Norway Spruce (Picea abies (L.) Karst) - is situated near the German/Czech border at 50°09′N and 11°52′E. Over the last years, flux measurements have been successfully performed on a 30 m research tower [e.g., *Klemm and Mangold*, 2001; *Burkard et al.*, 2002]. Through extensive quality assessment [*Foken and Wichura*, 1996] the applicability of eddy covariance techniques has been confirmed over the heterogeneous terrain of the "Fichtelgebirge" mountains. For example, during the three-week PANIC

---

[1] Bayreuth Institute of Terrestrial Ecosystem Research, University of Bayreuth, Bayreuth, Germany.

[2] Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, Giessen, Germany.

[3] Now at Institute of Landscape Ecology, University of Münster, Münster, Germany.

0094-8276/03/2003GL017854$05.00

campaign, 78% of the absolute mean vertical winds $\langle w \rangle$ were below 0.1 m s^{-1}, and 95% below 0.15 m s^{-1}. A subset of 358 vertical wind velocities from disjunct sampling on May 25, 2002 (see below for details) yielded a mean vertical wind velocity of -0.03. These results are a rather good approximation of the assumption of $\langle w \rangle = 0$. Stationarity tests for the wind field confirmed the validity of the steady-state assumption. However, since we do not measure particulate compound concentrations with the TOF-MS, it is difficult to test the stationarity of the concentration field with conventional tests. For particulate nitrate, we tried to emulate a widely used stationarity test by comparing the dispersion of normalized peak areas (see below for details) of the total sample and the average of the dispersions of normalized peak areas of six subsamples and obtained a difference of 30%. With this difference, a measurement is still considered to be stationary.

[6] An ultrasonic anemometer (YOUNG 81000, R. M. Young) was mounted 22 m above ground in the SE-corner of the tower. Wind vectors were acquired with a time resolution of 10 Hz.

[7] Next to the tower, a time-of-flight mass spectrometer (TOF-MS, LAMPAS 2) was operated to analyze the chemical composition of individual ambient aerosol particles. For a detailed description of this instrument see *Trimborn et al.* [2000]. Particles were introduced into the mass spectrometer through stainless steel tubing (ID 2.1 mm) ending next to the measuring region of the ultrasonic anemometer. The flow rate through the tubing was 1.6 l min^{-1}, and particles were sampled directly into the TOF-MS. Particle sizing was accomplished through time-of-flight measurement of the aerodynamic particle diameter. This information was also used by an active-triggering circuit [*Hinz et al.*, 2000] to ionize detected particles through laser desorption ionization (LDI). TOF-MS data acquisition was synchronized with the particle flux system. The travel time of particles from the sonic anemometer through the sampling line to the mass spectrometer was accounted for by subtracting a constant time lag of 4.1 s deduced from theoretical considerations of the flow dynamics in the sampling line.

[8] In order to deduce concentrations of particulate components from characteristic peak areas of single particle mass spectra, two ways of reducing variations of mass spectra due to varying particle composition and analysis conditions (inter-particle variability) have been proposed. *Gross et al.* [2000] suggest to normalize peak areas with the total peak area of the mass spectrum while *Johnston and Wexler* [1995] average information from several mass spectra. We combined both concepts and extended the averaging routine using Monte-Carlo type simulations (MCS) to yield a statistical interpretation of the mean normalized peak area of a given particle population for a specific compound [*Held et al.*, 2002]: (1) An individual particle is chosen randomly from the particle population and (2) combined with a second randomly chosen particle to calculate the mean normalized peak area (npa) of these two particles. Then, (3) another particle is randomly chosen to calculate the new mean npa of this new subsample. (4) Step (3) is repeated until all particles of the particle population have been combined, yielding averaged npa values of a specific compound for different subsample sizes. The entire procedure (1–4) is repeated very often (e.g., 10.000 times). As a result, for any subsample size (e.g., n = 3), a mean value and standard deviation of the 10.000 mean npa values is created.

[9] Single particle mass spectra were separated into virtual reservoirs of updraft (VUR) and downdraft (VDR) particles. This post-processing decision based on the vertical wind vector is similar to a valve in conventional eddy accumulation systems switching between updraft and downdraft reservoirs. However, as it is no hardware component of the setup, the decision is not irreversible as in true eddy accumulation systems. In order to sample proportionally to the vertical wind velocity, the separation procedure in eddy accumulation comprises a weighting routine depending on the magnitude of the vertical wind component.

[10] The flux of a chemical compound can be determined using the fundamental eddy accumulation equation [*Desjardins*, 1977]

$$F_c = \left\langle w^+ \cdot c_{up} \right\rangle + \left\langle w^- \cdot c_{down} \right\rangle \tag{1}$$

with F_c flux of compound c [nmol m^{-2} s^{-1}], w^+ updraft vertical wind component [m s^{-1}], w^- downdraft vertical wind component [m s^{-1}], c_{up} concentration of compound c in updraft particle [nmol m^{-3}], c_{down} concentration of compound c in downdraft particle [nmol m^{-3}], and brackets $\langle\rangle$ denoting averages over a given period of time.

[11] Peak area information from single particle mass spectra can theoretically be converted into ambient concentrations using relative sensitivity factors, RSF [*Mansoori et al.*, 1994; *Gross et al.*, 2000], for individual compounds, which are generally unknown. However, when sampling chemically similar aerosol particles under identical conditions, i.e., with the same instrument on the same day, we can assume a constant RSF for each individual compound. The validity of this concept has been shown for concentration ratios such as NO_3^-/NH_4^+ [*Held et al.*, 2002], but it can also be applied to single species such as NO_3^-. In this study, we assume a constant nitrate RSF for each particle sampled during the averaging period of a flux direction determination. The mean concentration of an individual compound, $\langle c \rangle$, equals the mean of the product of the normalized peak areas, npa, and the constant relative sensitivity factor, RSF.

[12] We obtain

$$\langle c \rangle = \langle npa \cdot RSF \rangle = \langle npa \rangle \cdot RSF \tag{2}$$

Applying the vertical wind velocity weighting routine yields

$$\langle w \cdot c \rangle = \langle w \cdot npa \cdot RSF \rangle = \langle w \cdot npa \rangle \cdot RSF \tag{3}$$

Combining equations (1) and (3) yields the true eddy accumulation equation adapted for IDES as

$$F_c = \left\langle w^+ \cdot npa_{up} \right\rangle \cdot RSF + \left\langle w^- \cdot npa_{down} \right\rangle \cdot RSF \tag{4}$$

with npa_{up} normalized peak area of compound c in updraft particle [−], npa_{down} normalized peak area of compound c in downdraft particle [−], RSF constant relative sensitivity factor for compound c [nmol m^{-3}].

[13] Dividing Equation (4) by the unknown, yet constant, relative sensitivity factor, RSF, yields the $\langle npa \rangle$-scaled transfer velocity of the chemical compound, v_t, as

$$v_t = F_c \cdot RSF^{-1} = \left\langle w^+ \cdot npa_{up} \right\rangle + \left\langle w^- \cdot npa_{down} \right\rangle \tag{5}$$

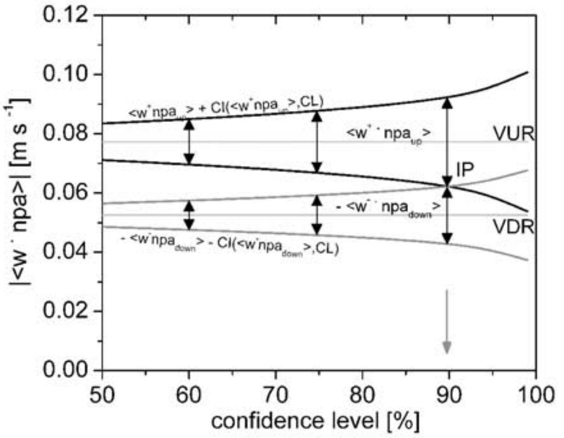

Figure 1. Means and confidence intervals of the weighted normalized peak areas of NO_3^- of the virtual updraft (VUR) and downdraft (VDR) reservoirs, respectively, for the particle population measured on May 25, 2002, at the "Waldstein" site: The confidence intervals begin to overlap at the intercept point IP at a confidence level CL of 89%.

The sign of v_t - or the flux direction—can be deduced from a comparison of the weighted normalized peak areas $\langle w^+ \cdot npa_{up}\rangle$ and $\langle w^- \cdot npa_{down}\rangle$ representing weighted relative compound concentrations in the virtual updraft and downdraft reservoirs, respectively.

[14] To determine the degree of confidence with which the resulting flux direction can be trusted, one has to consider the confidence intervals CI (Figure 1) within which the true value lies with a certain confidence (confidence level CL). The confidence intervals are obtained for VUR and VDR separately through Monte-Carlo type simulation. For any given confidence level, we compare the confidence intervals of $\langle w^+ \cdot npa_{up}\rangle$ and $\langle w^- \cdot npa_{down}\rangle$, respectively. The mean VUR and VDR weighted normalized peak areas are realizations of an averaging process of a subsample of the total population, i.e., the "real" mean weighted normalized peak area of the total population might deviate from the measured value, with its maximum deviation (i.e. the confidence interval) depending on the confidence level. As long as the confidence intervals of the virtual updraft and downdraft reservoirs do not overlap, the mean weighted normalized peak areas $\langle w^+ \cdot npa_{up}\rangle$ and $\langle w^- \cdot npa_{down}\rangle$ are different with a given confidence, yielding the respective flux direction according to Equation 5. The difference $\langle w^+ \cdot npa_{up}\rangle - (-\langle w^- \cdot npa_{down}\rangle)$ corresponds to the $\langle npa\rangle$-scaled transfer velocity, v_t, which is not the physical transfer velocity. By increasing the confidence level, the confidence intervals become larger until we finally arrive at a confidence level, where the confidence intervals for $\langle w^+ \cdot npa_{up}\rangle$ and $\langle w^- \cdot npa_{down}\rangle$ begin to overlap. It is not possible to determine the flux direction at higher confidence levels because the mean weighted normalized peak areas in the virtual updraft and downdraft reservoirs may equal each other in the overlap region.

3. Results

[15] TOF-MS measurements conducted in February 2000 set the basis for the following considerations leading to the determination of the particulate NO_3^- flux direction measured in May 2002. As a direct quantification of compounds in aerosol particles is not possible from mass spectra obtained by LDI, we applied averaging and normalizing of peak areas to deduce relative concentrations of specific compounds such as nitrate. In single particle mass spectra, nitrate exhibits two characteristic peaks in the negative spectra at the mass/charge ratios (m/z) 46 (NO_2^-) and 62 (NO_3^-) [e.g., *Noble and Prather*, 1996; *Murphy and Thomson*, 1997; *Trimborn et al.*, 2000]. For each individual particle, the peak areas at m/z = 46 and 62 are added up and then divided by the total peak area of the negative spectra yielding the normalized peak area, npa. In order to compute the relative NO_3^- concentration, all npa values of the particle population are averaged. Earlier studies showed that 1000 single mass spectra yield a representative sample of the ambient particle population. Therefore, the relative nitrate concentration of the total population can be determined by averaging the normalized nitrate peak areas of these 1000 particles. For subsamples with less than 1000 particles, we calculate confidence intervals of the relative nitrate concentration using Monte-Carlo-type simulations as described above. Then, each confidence interval represents the maximum deviation of the subsample concentration from the mean concentration of the total population due to non-representative sampling.

[16] In Figure 2, maximum deviations of the relative nitrate concentration are displayed for four different particle populations measured in February 2000 at a confidence level of 95%. The 95% confidence interval (or maximum deviation) is narrowing with increasing size of the subsample. Since the pattern of this variation is very similar in all populations, we suggest to introduce a universal confidence matrix for this particular chemical compound. By calculating confidence intervals of the relative nitrate concentration for varying confidence levels, we obtain Figure 3.

[17] Maximum deviations of relative nitrate concentrations are displayed for varying confidence level (ordinate) and subsample size (abscissa). The maximum deviation from the relative concentration of the total population becomes largest for small subsample sizes, and high confi-

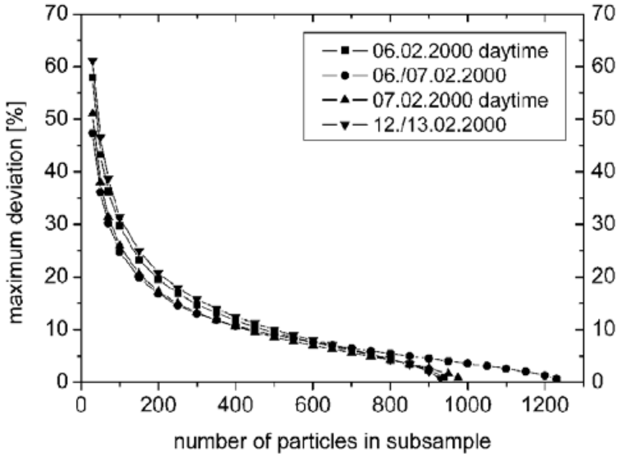

Figure 2. Maximum deviations (confidence intervals) of the relative NO_3^- concentration depending on the number of particles in a subsample at a confidence level of 95%: Displayed are four different particle populations measured in February 2000.

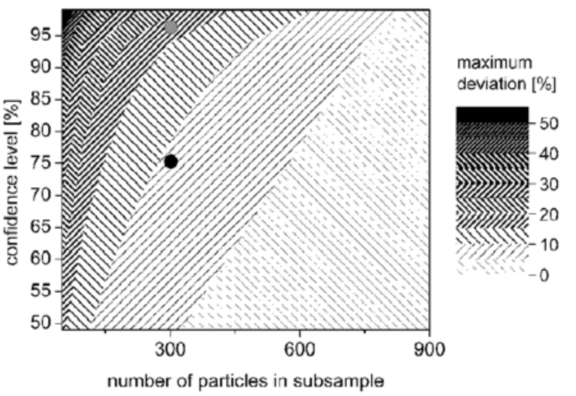

Figure 3. Universal confidence matrix for relative NO_3^- concentrations: The fill pattern indicates the maximum deviation of the relative NO_3^- concentration at a certain confidence level (ordinate) for a certain number of analyzed particles (abscissa). The dots are examples for a sample of 300 particles at confidence levels of 75% (black) and 95% (grey), respectively.

dence levels. For example, if we analyze 300 particles we can expect a deviation between 5% and 10% with a confidence of 75% (black dot), while the deviation might be as large as 15% to 20% with a confidence of 95% (grey dot).

[18] In order to determine the flux direction of particulate nitrate, we need to know the number of particles and the mean values of the relative nitrate concentration in the virtual updraft and downdraft reservoirs, respectively. For example, on May 25, 2002, we analyzed 172 particles in the VUR and 186 particles in the VDR during a 4h period, yielding weighted relative nitrate concentrations of 0.0773 in the VUR and 0.0525 in the VDR, respectively. According to Equation (5), the corresponding nitrate flux for this time period is directed from the surface to the atmosphere, i.e. nitrate emission. To obtain the confidence level of this statement, we reconsider Figure 1. In our case on May 25, we could determine particulate nitrate emission with a confidence of 89%. In the context of atmospheric nitrogen input into ecosystems, particulate nitrate emission contradicts the general observation of total nitrogen deposition. With the present data set we are not able to identify the process that might lead to the statistically significant emission of particulate NO_3^- on that day.

4. Concluding Remarks

[19] We presented a statistical procedure to determine the flux direction of individual particulate compounds from single particle analysis. The first experimental realization of this method was limited by several technical problems. For example, it was intended to operate the mass spectrometer on a tower platform 5 m below the ultrasonic anemometer. However, due to adverse weather conditions it was impossible to lift the mass spectrometer on the tower, and a relatively long sampling line had to be used. Therefore, the number of analyzed particles was smaller than expected, introducing a greater statistical uncertainty, and the correlation of individual particles and the vertical wind component is more difficult. Also, the sampling line could introduce a particle size bias due to size-dependent wall losses, however, we consider this effect to be small for the measuring range of the TOF-MS. Our results suggest that a combination of disjunct eddy sampling and single particle analysis bears a great potential to directly measure turbulent vertical fluxes of particulate compounds as soon as methods have been devised to determine compound specific RSF values in conjunction with TOF-MS measurements.

[20] **Acknowledgments.** This work was funded by the German federal research ministry (BMBF) through grants PT BEO 51-0339476 C and PT UKF 07ATF25. We appreciate the help and support of G. Müller and M. Rader during the field experiment.

References

Burkard, R., W. Eugster, T. Wrzesinsky, and O. Klemm, Vertical divergences of fogwater fluxes above a spruce forest, *Atmos. Res.*, *64*, 133–145, 2002.

Buzorius, G., Ü. Rannik, J. M. Mäkelä, T. Vesala, and M. Kulmala, Vertical aerosol particle fluxes measured by eddy covariance technique using condensational particle counter, *J. Aerosol. Sci.*, *29*, 157–171, 1998.

Buzorius, G., Ü. Rannik, J. M. Mäkelä, P. Keronen, T. Vesala, and M. Kulmala, Vertical aerosol fluxes measured by the eddy covariance method and deposition of nucleation mode particles above a Scots pine forest in southern Finland, *J. Geophys. Res.*, *105*, 19,905–19,916, 2000.

Desjardins, R. L., Description and evaluation of sensible heat flux detector, *Bound. Lay. Meteorol.*, *11*, 147–154, 1977.

Dorsey, J. R., E. Nemitz, M. W. Gallagher, D. Fowler, P. I. Williams, K. N. Bower, and K. M. Beswick, Direct measurements and parameterisation of aerosol flux, concentration and emission velocity above a city, *Atmos. Environ.*, *36*, 791–800, 2002.

Foken, Th., and B. Wichura, Tools for quality assessment of surface-based flux measurements, *Agric. For. Meteorol.*, *78*, 83–105, 1996.

Gallagher, M. W., K. M. Beswick, J. Duyzer, H. Westrate, T. W. Choularton, and P. Hummelshoj, Measurements of aerosol fluxes to Speulder forest using a micrometeorological technique, *Atmos. Environ.*, *31*, 359–373, 1997.

Gross, D. S., M. E. Gaelli, P. J. Silva, and K. A. Prather, Relative sensitivity factors for alkali metal and ammonium cations in single-particle aerosol time-of-flight mass spectra, *Anal. Chem.*, *72*, 416–422, 2000.

Held, A., K.-P. Hinz, A. Trimborn, B. Spengler, and O. Klemm, Chemical classes of atmospheric aerosol particles at a rural site in Central Europe during winter, *J. Aerosol Sci.*, *33*, 581–594, 2002.

Hinz, K.-P., A. Trimborn, and B. Spengler, Instrumental improvements in on-line laser mass spectrometry of aerosols, Proceedings of the 48th ASMS Conference on Mass Spectrometry and Allied Topics, Long Beach, 2000.

Johnston, M. V., and A. S. Wexler, MS of individual aerosol particles, *Anal. Chem.*, *67*, 721A–726A, 1995.

Klemm, O., and A. Mangold, Ozone Deposition at a Forest Site in NE Bavaria, *Water Air Soil Pollut. Focus*, *1*, 223–232, 2001.

Lenschow, D. H., J. Mann, and L. Kristensen, How long is long enough when measuring fluxes and other turbulent statistics?, *J. Atmos. Oceanic Tech.*, *11*, 661–673, 1994.

Mansoori, B. A., M. V. Johnston, and A. S. Wexler, Quantitation of ionic species in single microdroplets by on-line laser desorption/ionization, *Anal. Chem.*, *66*, 3681–3687, 1994.

Murphy, D. M., and D. S. Thomson, Chemical composition of single aerosol particles at Idaho Hill: Negative ion measurements, *J. Geophys. Res.*, *102*, 6353–6368, 1997.

Noble, C. A., and K.-A. Prather, Real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles, *Environ. Sci. Technol.*, *30*, 2667–2680, 1996.

Rinne, H. J. I., A. C. Delany, J. P. Greenberg, and A. B. Guenther, A true eddy accumulation system for trace gas fluxes using disjunct eddy sampling method, *J. Geophys. Res.*, *105*, 24,791–24,798, 2000.

Trimborn, A., K.-P. Hinz, and B. Spengler, Online analysis of atmospheric particles with a transportable laser mass spectrometer, *Aerosol Sci. Technol.*, *33*, 191–201, 2000.

Wexler, A., and K. Prather, Introduction: Online single particle analysis, *Aerosol Sci. Technol.*, *33*, 1–2, 2000.

A. Held and O. Klemm, Institute of Landscape Ecology, University of Münster, 48149 Münnster, Germany. (andreas.held@uni-muenster.de)

K.-P. Hinz, B. Spengler, and A. Trimborn, Institute of Inorganic and Analytical Chemistry, Justus Liebig University Giessen, 35392 Giessen, Germany.