Atmospheric Research 102 (2011) 49–56

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Characterization of vertical aerosol flows by single particle mass spectrometry for micrometeorological analysis

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ARTICLE INFO

Article history:
Received 15 July 2010
Received in revised form 4 May 2011
Accepted 4 May 2011

Keywords:
Mass spectrometry
Single particle analysis
Micrometeorology
Environmental analysis

ABSTRACT

A single particle mass spectrometer LAMPAS 2 (Laser Mass Analyzer for Particles in the Airborne State) was combined with an ultrasonic anemometer to provide a measurement system for monitoring environmental substance exchange as caused by emission/deposition of aerosol particles. For this study, 681 mass spectra of detected particles were sorted into groups of similarity by a clustering algorithm leading to five classes of different particle types. Each single mass spectrum was correlated to corresponding anemometer data (vertical wind vector and wind speed) in a time-resolved analysis. Due to sampling constraints time-resolution was limited to 36 s, as a result of transition time distributions through the sampling tube. Vertical particle flow (emission/deposition) was determined for all particles based on these data as acquired during a measuring campaign in Giessen, Germany. For a selected particle class a detailed up- and downwards flow consideration was performed to prove the developed approach. Particle flow of that class was dominated by an emission trend as expected. The presented combination of single-particle mass spectrometry and ultrasonic anemometry provides for the possibility to correlate chemical particle data and wind data in a distinct assignment for the description of turbulent particle behavior near earth surface. Results demonstrate the ability to apply the method to real micrometeorological systems, if sampling issues are properly considered for an intended time resolution.

1. Introduction

The global ecosystem is affected by interactions with natural and anthropogenic matter. Such material can be placed into the environment as gas, fluids or particles. Studies showed both effects, emission of particles from the earth's surface into the atmosphere and deposition of particles onto the surface. Particles are known to modify cloud formation (Henning et al., 2002; Ruehl et al., 2008; Lohmann and Feichter, 2005), the radiation budget of the atmosphere and by that influence climate and global warming (Seinfeld, 2008; Poeschl, 2005). Transport of chemical compounds via particles has been shown to vary the nutrient and pollutant budgets of the ecosystem (Wesely and Hicks, 2000). A detailed determination of matter deposition and emission is needed. Neither chemical analysis of particulate matter nor determination of transportation paths and mechanisms alone provide a complete description of the matter flows. Source tracing, lifetime studies, chemical modification analysis and flight path studies of particles are important additional sources of information in this context. Correlation of particle composition with air parcel transportation trajectories across Europe confirmed the link between point of origin, particle flight paths and chemical composition of particles (Trimborn et al., 2002). More regional approaches of source and flight path determination (Rhoads et al., 2003; Bein et al., 2007)

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doi:10.1016/j.atmosres.2011.05.017

demonstrated the possibility to allocate particle classes to their sources by correlating horizontal wind data with the appearance of particles.

Meteorological and micrometeorological methods offer a number of possibilities for exact local determination of vertical emission and deposition processes. So-called 'direct' and 'indirect' approaches were used e.g. for determination of biosphere–atmosphere exchange of nitrogen species (Sutton et al., 2007). An 'indirect' approach is the gradient technique (Fowler et al., 2001) where the gradients of e.g. temperature and particle density were correlated to determine the vertical particle flux. Disadvantages of this method are the requirement of several measurement points and the missing identification of particle components. A 'direct' approach is the irregular disjunct eddy sampling (IDES) (Held et al., 2003) which is based on the disjunct eddy sampling method (Rinne et al., 2000). IDES combines laser desorption ionization time-of-flight mass spectrometry (LDI-TOF-MS) of particles and the eddy covariance method (Stull, 1999). In a study of Nemitz et al. (2008), an ultrasonic anemometer for wind data determination was combined with an aerosol mass spectrometer (Q-AMS, Aerodyne Research Inc.) for particle detection. A particle beam was introduced into the mass spectrometer for continuous and quantitative detection of particles components. Determination of turbulent fluxes of selected chemical constituents (e.g. nitrate, ammonia, sulfate) was performed by analyzing the correlation of mass spectrometric information and anemometer wind data.

A new approach is described in the following, also based on the proposal of Held et al. (2003). An ultrasonic anemometer was used to determine the vertical wind vectors. An on-line single particle mass spectrometer LAMPAS 2 (Laser Mass Analyzer for Particles in the Airborne State) (Trimborn et al., 2000) provided identification and characterization of detected single particles. In contrast to the study of Nemitz et al. (2008), not continuous particle matter beams or short, continuous particle beam packets were analyzed but individual particles. This provides for analysis of selected particles in combination with their corresponding wind data. The single particle data set was filtered by cluster analysis to group chemically similar particles into separated classes. This analysis provided a time-resolved observation of the appearance of similar single particles in combination with an individual particle/wind data correlation. This newly developed approach of combined single-particle mass spectrometry with wind measurements provides for a distinct assignment of single particle and wind data. Thus, a detailed investigation of turbulent environmental exchange processes near the earth surface for individually particles as well as for groups of chemically similar particles can be performed. Additionally, further investigations of particle fluxes will become possible by the use of combined data sets in micrometeorological methods.

2. Instrumentation and methods

LAMPAS 2 is a mobile, bipolar on-line laser mass spectrometer (Trimborn et al., 2000). It provides for chemical and physical characterization of individual airborne particles in the sub-micron and super-micron size range. The instrument uses an impact-free particle inlet system with a differentially pumped nozzle/skimmer system for introduction of particles into the mass spectrometer. Two parallel cw laser beams (wavelength $\lambda = 532$ nm) are used to detect the particles. Particle velocities are determined based on crossing time between the two laser beams. The aerodynamic diameter of the particle can be derived from particle velocities (Hinds, 1999). An actively triggered UV laser pulse ($\lambda = 337$ nm) evaporates and ionizes the particles. Subsequently a bipolar time-of-flight mass spectrometer analyzes the generated ions.

Wind direction data were recorded by an ultrasonic anemometer (Model 81000, R.M. Young Company, Traverse City, MI, USA) with a resolution of 10 Hz. In addition wind speed and temperature were measured. Accuracy of the anemometer was $\pm 1\%$ (min. ± 0.05 m s^{-1}) for wind speed measurements and ± 2 degrees for wind direction determinations.

An exposed gallery on the west side of the institute building in Giessen (Institute of Inorganic and Analytical Chemistry, 50°34′N, 8°40′E) was used as a measurement site. The metal lattice gallery protrudes the edge of the building by 2.05 m. The building is located in a remote housing area without urban traffic. The experiment was performed 6.85 m above ground on 6th December 2006, 10:22–19:24 h. The measurement day was a cold, clear winter day with low wind movements. The particle inlet was fixed 25 cm beside the ultrasonic anemometer in order to avoid distortion of wind data recording. Wind flow variations are known to be rare within such short sections, so spatial inaccuracies originating from this offset could be neglected. The inlet enabled a horizontal, equal inflow of up- and downward streaming particles. A laminar flow of 1.6 L min^{-1} transmitted the particles to the LAMPAS 2 through a 10.53 m long flexible tube (TYGON®-R3603; i.d. 8 mm). Maximum transition time of the particles was determined as 36.11 s by calculation of flow dynamics in the sampling tube (Hinds, 1999; Willeke and Baron, 1993). This value takes into account the different radial flow velocities through the tube for all detected particle sizes. Wind data of an interval of 36.11 s were averaged to account for particle transition time distributions. These values were used for correlation of wind data and corresponding particles. A radio time receiver synchronized the internal clocks of the computers (LAMPAS 2 and wind data acquisition) every 5 min.

In the first step of data evaluation, particle mass spectra obtained by LAMPAS 2 were classified by means of a fuzzy clustering algorithm (Hinz et al., 1999). The algorithm provides a chemical assignment of particle classes (groups of chemically similar particles) and their abundances. It calculates the membership degree of individual particles to classes by determination of degrees of similarity. Based on these membership degrees a particle can be assigned to one or more classes. The sum of all membership degrees per particle is always 1.0 while the sum of all membership degrees per class corresponds to the class abundance of the entire particle population. Another feature of the classification software is that classes can be visualized as spectra patterns. These patterns provide for a chemical interpretation of particle classes.

In the following study particles (i.e. mass spectra) were sorted with respect to the measured vertical wind data in a second step of data evaluation. These correlations were performed class by class and only for particles with a membership degree of more than 60% ('main particles') to their class. This ensured that their compositions matched the

composition as expressed in the mass spectra patterns. Each of these selected particles had a timestamp from its mass spectral acquisition. This timestamp was corrected for the mean transition time a particle needs between sampling point and mass spectrometer. The corresponding averaged wind data were assigned to the particles by their timestamp of acquisition. The combination thus provided for a time-resolved description of particle appearance, particle flight direction and speed.

3. Results and discussion

3.1. Mass spectra analysis

A number of 681 particles was detected by the LAMPAS 2 instrument during the measuring time of 9 h and 2 min. Particle diameters ranged between 0.2 μm and 2 μm. A bipolar mass spectrum of a single particle is shown in Fig. 1 as an example. The diameter of this particle was determined as 1.2 μm.

The negative-ion spectrum is dominated by carbon cluster ions, also presented in the positive-ion spectrum (C_n^-/C_n^+, $n=2$–9, $m/z=24$, 36, 48…). The negative-ion spectrum additionally contains anion signals derived from hydroxyl (OH^-, $m/z=17$) and nitrate ions (NO_2^-, $m/z=46$, NO_3^-, $m/z=62$). Dominating peaks in the positive-ion spectrum are sodium (Na^+, $m/z=23$), potassium (K^+, $m/z=39$), calcium (Ca^+, $m/z=40$) and corresponding oxide (CaO^+, $m/z=56$) and hydroxide ($CaOH^+$, $m/z=57$), respectively.

Particle mass spectra classification using the fuzzy clustering algorithm resulted in five chemical particle classes. Their spectra patterns are shown in Fig. 2.

Mass spectra patterns of negative and positive-ions were normalized to highest ion signal for each pattern. The particle classes differ from each other especially by the characteristics of carbon cluster patterns (C_n^-/C_n^+, $n=2,3,4…$, $m/z=24$, 36, 48…) and by the intensities of salt ions (e.g. Na^+, $m/z=23$, K^+, $m/z=39$; Ca^+, $m/z=40$, NO_2^-, $m/z=46$, NO_3^-, $m/z=62$, HSO_4^-, $m/z=97$) (Trimborn et al., 2002 ; Vogt et al., 2003). The patterns of the first three classes (Fig. 2a, b, c) are dominated by the sodium peak (Na^+, $m/z=23$). These classes look rather similar if intensity variations are neglected. On closer examination these classes depict an obvious increase of carbon cluster intensities in the positive-ion spectra as well as a decrease of salt ion intensities in the negative-ion spectra, going from class 1 to class 3. Fig. 2d) shows class 4 ('carbon 3 + salt') with distinct carbon clusters in positive and in negative-ion spectra (C_n^-/C_n^+, $n^-=2$–7, $n^+=2$–11, $m/z=24$, 36, 48…) (Hinz et al., 2005). In class 5 ('salt') the main positive-ion signal is from potassium (K^+, $m/z=39$) (Held et al., 2002). Sodium, carbon clusters and organics (e.g. $C_3H_5^+$, $m/z=41$, $C_3H_7^+$, $m/z=43$, $C_4H_7^+$, $m/z=55$) (Kolaitis et al., 1989) are also represented (Fig. 2e). The negative-ion spectrum of this class shows peaks at a mass-to-charge ratio of 79, 80 and 81 in addition to salt (Cl^-, $m/z=35$) and carbon patterns. Peak combinations suggest presence of phosphate (PO_3^-, $m/z=79$ and $H_2PO_4^-$, $m/z=97$) and sulfate (SO_3^-, $m/z=80$, HSO_3^-, $m/z=81$ and HSO_4^-, $m/z=97$). Class abundances of these five classes in the measured particle population are listed in Table 1.

A high abundance of particles with a high carbon and salt content was expected due to the chosen measurement-location (urban periphery and car park in close proximity). These particles probably originated from fuel combustion processes due to urban traffic (Vogt et al., 2003). Typical carbon cluster peaks were found in different intensities in all classes. In comparison to exhaust studies (Shields et al., 2007; Toner et al., 2006) the calcium was detected in low intensities in the mass spectra patterns. Nevertheless, these patterns are assignable to exhaust particles resulting from calcium/phosphate containing engine oil lubrication formation. Dominance of certain components in mass spectra patterns is reflected in naming of the classes. Class 5 particles for example ('salt') are most probably ubiquitary salt particles with typical components such as potassium and phosphate (Trimborn et al., 2002). Classification results reflect these expectations as shown.

3.2. Deposition/emission of particles

Among all detected particles, 495 had a membership degree of more than 60% ('main particles') to one of the determined classes. Time-resolved detection of these particles is shown in Fig. 3. The graph depicts the occurrence of these particles in combination with their corresponding averaged vertical wind speed and direction. On average, particles were detected at a wind speed of $+0.07\ m\ s^{-1}$ ($\pm 0.13\ m\ s^{-1}$); maximum up- and downdraft speeds were $+0.70\ m\ s^{-1}$ ($\pm 0.48\ m\ s^{-1}$) and

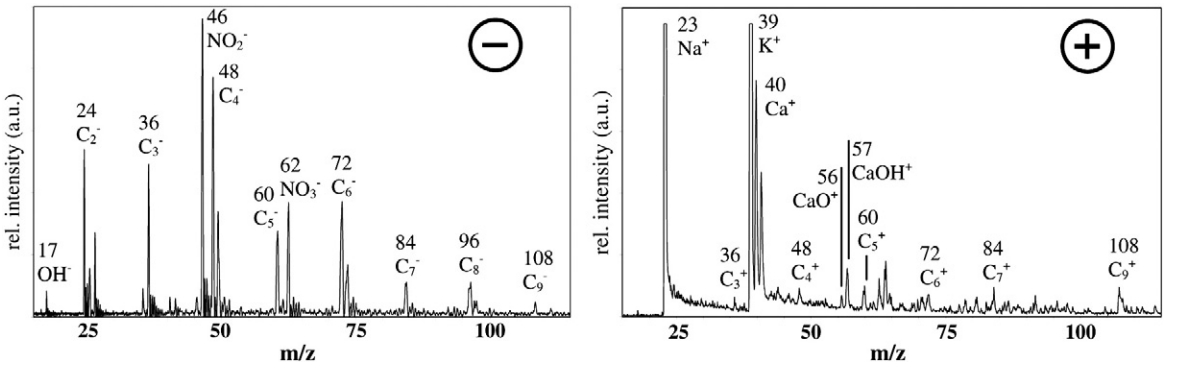

Fig. 1. Negative-ion and positive-ion mass spectrum of a single aerosol particle from ambient air (particle diameter: 1.2 μm).

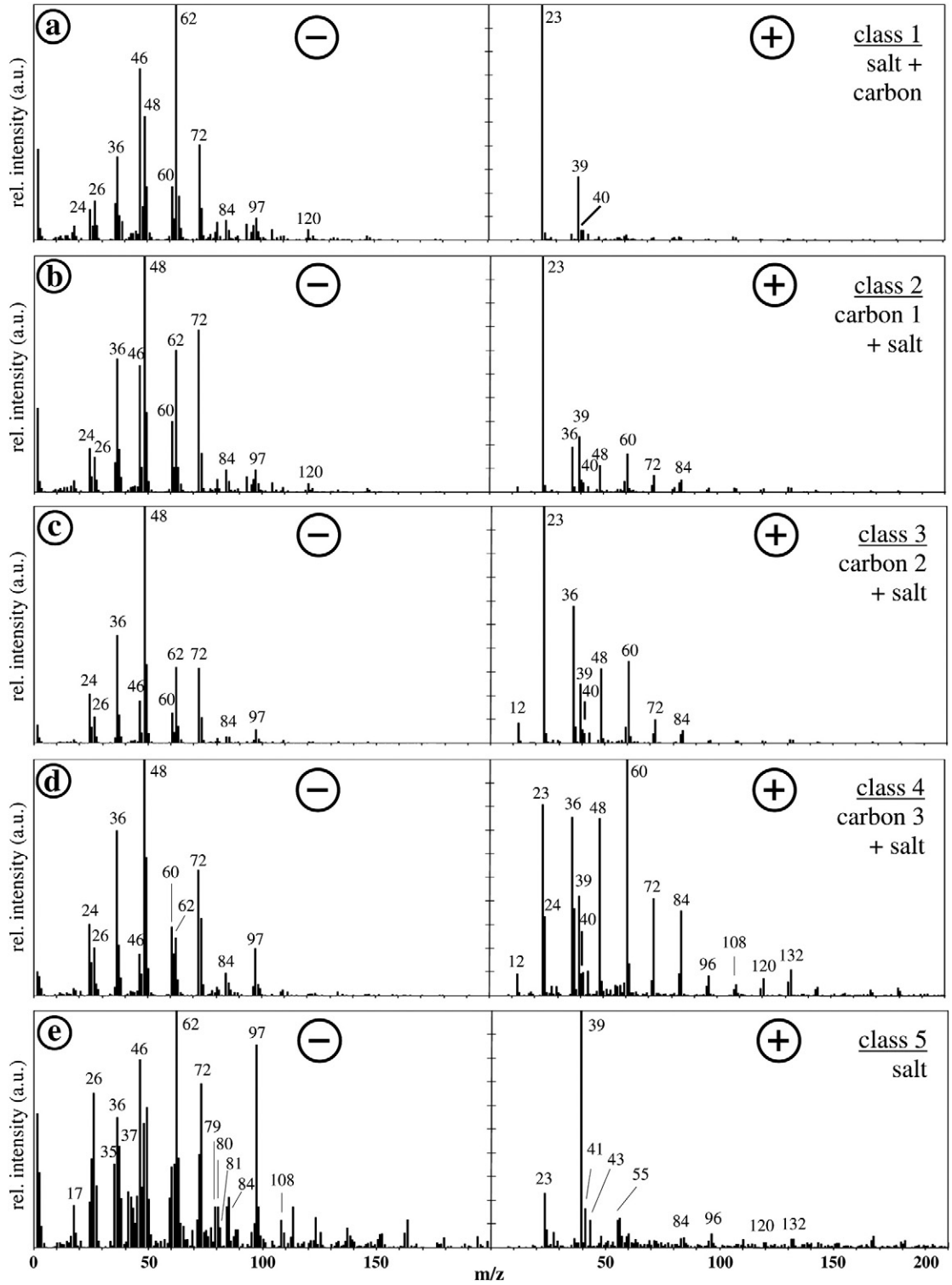

Fig. 2. a–e: Representative spectra patterns calculated via fuzzy clustering; negative-ion and positive-ion patterns were normalized to highest ion signal for each pattern.

$-0.31\ m\ s^{-1}$ ($\pm 0.66\ m\ s^{-1}$), respectively. 341 of 495 main particles were located in updraft situation, 154 in downdraft situation. The cross-hatched bars indicate technical maintenance periods without data collection.

A possible correlation between particle composition and vertical wind direction was investigated by analyzing the flow behavior of particle classes individually. The numbers of 'main particles' per class detected during

Table 1
Class abundance of 681 detected particles determined by fuzzy clustering.

Chemical particle class	Class abundance [%]
Class 1: salt + carbon	59.2
Class 2: carbon 1 + salt	16.4
Class 3: carbon 2 + salt	12.2
Class 4: carbon 3 + salt	7.3
Class 5: salt	4.9

Table 2
Number of 'main particles' per class detected during updraft or downdraft situation.

Chemical particle class	Number of 'main particles'	
	up	down
Class 1: salt + carbon	227	95
Class 2: carbon 1 + salt	34	24
Class 3: carbon 2 + salt	41	19
Class 4: carbon 3 + salt	20	11
Class 5: salt	19	5

updraft or downdraft situation were determined as listed in Table 2.

Higher numbers of particles were observed in updraft situation than in downdraft situation both, in total and within individual classes. Immediate influences of the surroundings could be minimized by the chosen measurement site. Due to the location close to a building, however, a higher percentage of updraft is anticipated due to thermal convection. In consequence, an increase in particle detection in updraft mode is expected.

Class 1 was selected for more detailed investigations because it covered the highest number of particles within the classification. All particles were removed from consideration which had a time lag of detection of less than 36.11 s to the previously detected particle. This was conducted to avoid overlapping of wind data intervals of adjacent particles and to ensure a distinct assignment of wind and particle data. Resulting total number of class 1 particles was 215. Among these particles, 157 were carried in updraft situation and 58 in downdraft situation.

Fig. 4 shows the size distribution for all detected particles as well as for class 1 particles and for class 1 particles detected during updraft and downdraft situation. Particle diameters ranged from 0.2 μm to 2 μm. Most particles had a diameter between 1.1 μm and 1.5 μm. Size distributions of particles detected during updraft and during downdraft situation showed no significant differences. For both categories the highest abundance of detected particles was found at a diameter of about 1.25 μm.

Fig. 5 shows a time-resolved chart of detected particles of class 1. Averaged vertical wind direction and speed were assigned to each detected particle. The mean averaged vertical wind speed was $+0.07\ m\ s^{-1}$ ($\pm 0.14\ m\ s^{-1}$).

The graph illustrates that the vertical wind was changing over the complete measuring period and no consistent flow direction of particles for a longer period was observed. For this reason the number of class 1 particles was determined per wind speed range ($\Delta v = 0.1\ m\ s^{-1}$) normalized to the total number of particles per wind speed range (Fig. 6).

Analysis of the relative abundance shows that the particle number concentration of class 1 particles is higher in updraft than in downdraft mode, indicating a matter emission situation. This implies that class 1 particles occurred in higher concentrations below measurement height (6.85 m) compared to higher levels. This observation is in good agreement with expectations. A positive averaged wind speed value for class 1 indicated an emission situation. Consideration of the other classes indicates an opposite (classes 2 and 3) or similar

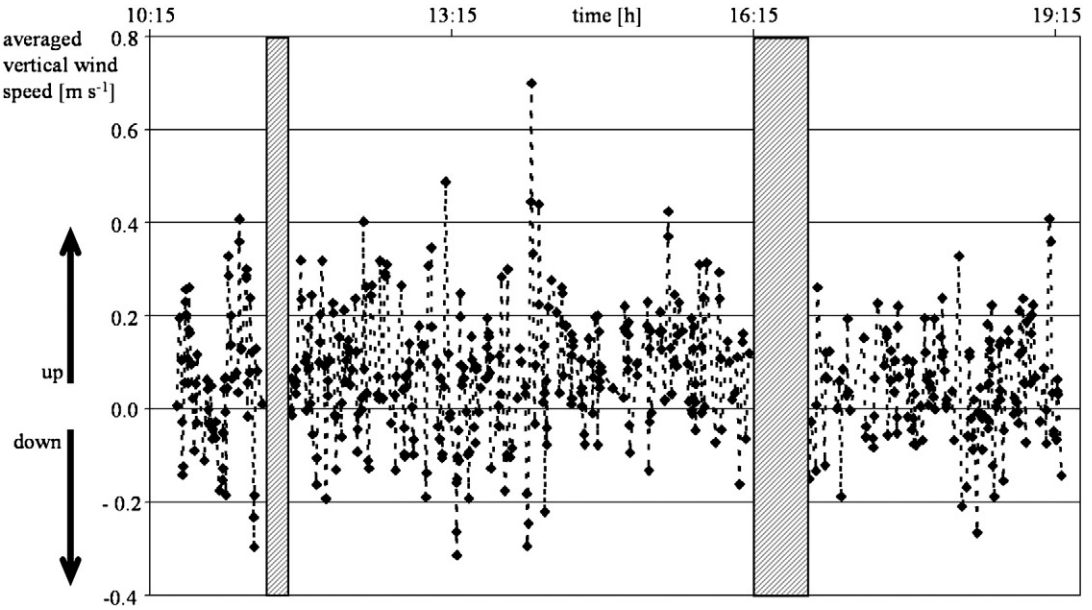

Fig. 3. Averaged vertical wind speed/direction of 'main particles' detected over time. Dots indicate individual particles detected by LAMPAS 2. Bars indicate instrumental maintenance periods.

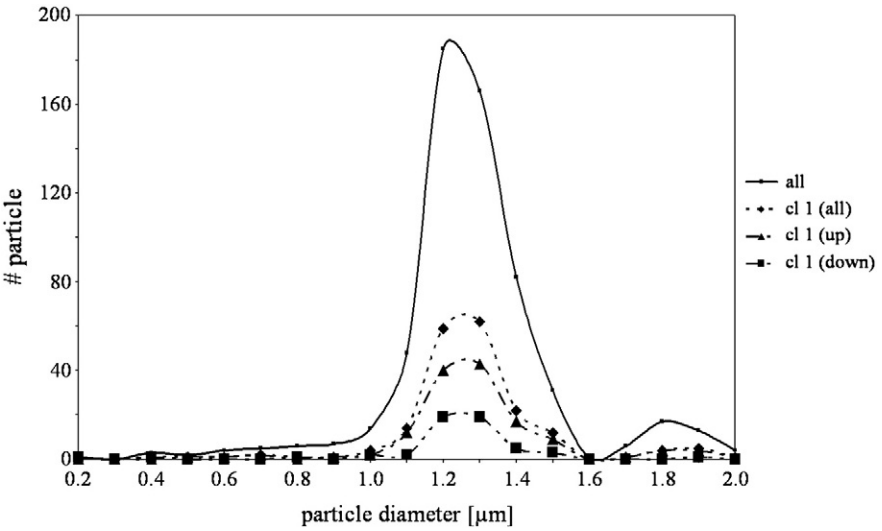

Fig. 4. Size distribution of detected ambient air particles: all (solid line), class 1 particles (dashed line; diamonds), class 1 particles in updraft (dashed line, triangles), class 1 particles in downdraft situation (dashed line, squares).

behavior (classes 4 and 5). Particle numbers, however, were too small for a reliable statistical analysis and require confirmation in future extended measurements.

4. Conclusions

The employed setup consisting of the mass spectrometer LAMPAS 2 and an ultrasonic anemometer has been shown to be well suited for single particle detection and wind measurements in parallel during a field measuring campaign. Off-line mass spectra classification via fuzzy clustering is a useful approach to separate particles of different compositions into specific classes. Averaged vertical wind vectors were assigned to each single particle of such a class. Emission and deposition flow behavior was characterized for individual particles. A selected class was investigated in more detail. An exact up- and downwards flow consideration was performed to prove the developed approach of the distinct assignment of wind and single particle data. More particles were carried by updraft than by downdraft in this class. The corresponding mean wind speed of the particles was positive, i.e. the situation was dominated by updraft. A normalization of data showed that the particle number concentration was higher in updraft than in downdraft.

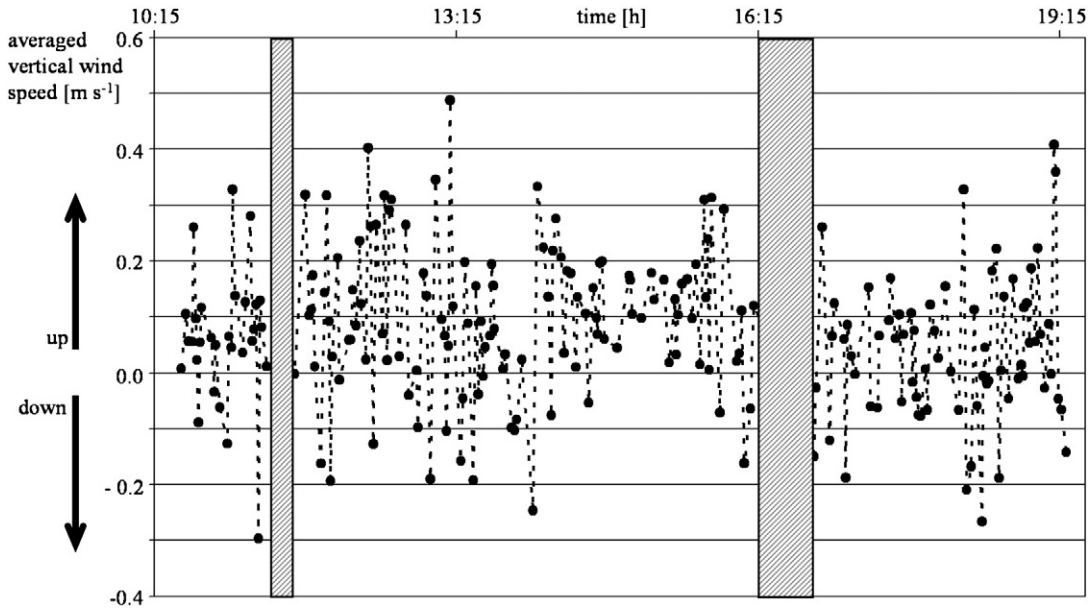

Fig. 5. Averaged vertical wind speed/direction of selected 'main particles' of class 1 ('salt + carbon') detected over time. Dots indicate individual particles detected by LAMPAS 2. Bars indicate instrumental maintenance periods.

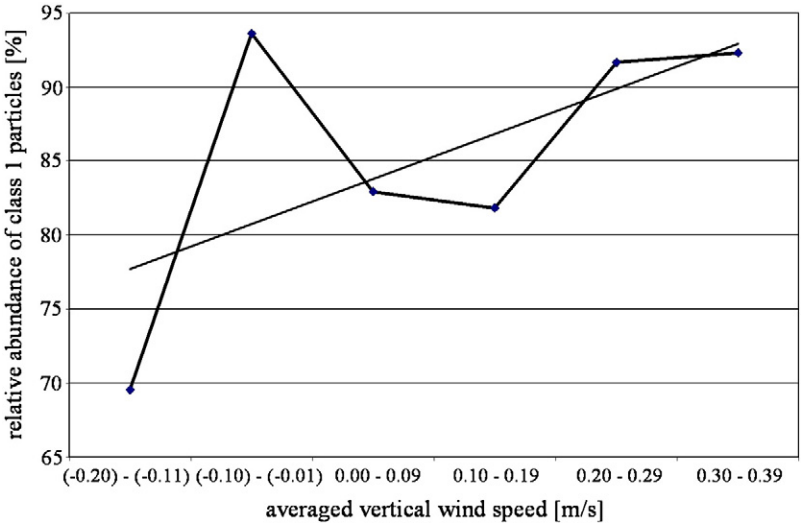

Fig. 6. Relative abundance of selected class 1 particles per vertical wind speed range. A trend line indicates the increased relative abundance at higher vertical speed in updraft.

With this newly developed approach, a method for direct correlation of wind data and single particle data with high time resolution is available for the description of turbulent particle behavior and investigation of environmental exchange processes. Results demonstrate the ability to apply the method to real micrometeorological systems, if sampling issues are considered with respect to an intended time resolution. Future experiments will cover larger data sets to increase precision of correlation results. Studies of correlations between particle and wind data alone are not sufficient to fully describe real environmental processes. Determination of emitted or deposited matter concentrations of selected substances is additionally required. With that, a combination with micrometeorological flux determination using the eddy covariance method will become possible. Such an approach can provide for an accurate determination of particle component fluxes in emission and deposition direction. This offers new possibilities for a detailed determination of environmental substance exchange.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft, Germany, (grant no. HI 857/4-1 and KL 623/8-1) and by the State of Hesse (LOEWE research focus AmbiProbe) is gratefully acknowledged.

This work is part of the dissertation of Elmar Gelhausen at the Justus Liebig University of Giessen.

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