

Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany

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Abstract

The chemical composition and chemically resolved size distributions of fine aerosol particles were measured at high time resolution (5 min) with a time-of-flight aerosol mass spectrometer (TOF-AMS) during the New Year's 2005 fireworks in Mainz, central Germany. In addition, particle number concentrations and trace gas concentrations were measured using a condensation particle counter (CPC) and a proton transfer reaction mass spectrometer (PTR-MS). The main non-refractory components of the firework aerosol were potassium, sulfate, total organics and chloride. Increased trace gas mixing ratios of methanol, acetonitrile, acetone and acetaldehyde were observed. Aerosol nitrate and ammonium concentrations were not significantly affected by the fireworks as well as the measured aromatic trace gases. The sub-micron aerosol concentrations peaked about 20 min after midnight with total mass concentrations larger than $600 \mu\text{g m}^{-3}$. The trace gas concentrations peaked about 30 min later. Using the sulfur-to-potassium concentration ratio measured in another fireworks aerosol, it was for the first time possible to estimate the relative ionization efficiency of aerosol potassium, measured with the TOF-AMS. Here we found a value of $\text{RIE}_K = 2.9$.

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1. Introduction

Festivities throughout the world are traditionally accompanied by loud and brightly colored pyrotechnic displays. The use of fireworks ranges from smaller scale local events such as birthdays or

weddings, up to nationwide celebrations, often commemorating specific historical events. In the United States for example, Independence Day (4 July) is celebrated with intensive firework displays. In France the revolutionary overthrow of monarchy and government is celebrated with fireworks on 14 July, whereas in the United Kingdom the failure of such an attempt is similarly feted on 5 November. In India, the festival of Divali ('festival of lights') is celebrated for several days during October/November using burning illuminations and fireworks. In many

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areas throughout the world New Year is celebrated with widespread pyrotechnical displays. One thing that all these fireworks have in common is that they emit trace gases into the atmosphere and generate dense clouds of smoke.

While toxic organic substances and heavy metals have been found only in low concentrations in firework products (Fleischer et al., 1999; Alenfelt, 2000), the extensive use of pyrotechnics during larger events typically causes significant short-term air quality degradation (Mandal et al., 1997; Perry, 1999; Ravindra et al., 2003; Kulshrestha et al., 2004), with possible impact on human health (Smith and Dinh, 1975; Clark, 1997). In addition, depending on the meteorological situation substantial visibility reductions can accompany fireworks in cities located in valleys or beneath inversion layers for time intervals up to several hours. Although many organic trace gas emissions have the potential to profoundly affect atmospheric chemistry (Williams, 2004 and references therein), the effect of inputs from fireworks on the global budget of species such as methanol and acetone has been estimated as negligible (Williams et al., 2005).

Very few measurements of fireworks aerosol with high time resolution are described in the literature. These cover particle size distribution measurements (Wehner et al., 2000), single particle mass spectrometry (Liu et al., 1997), black carbon concentration measurements (Babu and Moorthy, 2001), and sampling of particles with a stacked filter unit and subsequent weighing and analysis by PIXE (Dutcher et al., 1999). However, most of these measurements were performed far away from the centers of activities, resulting in a measurement of the advected smoke cloud. Measurements of aerosol and trace gases associated with New Year's fireworks are an excellent test of instrumentation with high time resolution. The emission is large and occurs at a well-defined point in time in the absence of complicating sunlight driven photochemistry.

Here we describe for the first time simultaneous measurements of particle number concentrations, size-resolved chemical composition of the non-refractory particle components, and organic trace gases with high time resolution (5 min and better). The measurements were performed in the center of firework activities on the south bank of the Rhine in Mainz, Germany (50°N, 8°W) during the New Year's festivities 2004/2005.

2. Experimental

2.1. Measurement site

The instruments used in this study were housed in a maintenance garage within one of the supports for the Theodor Heuss bridge, which crosses the Rhine river close to the center of Mainz, a small city (population 120 000) in central Germany. The aerosol and gas inlets were located at a height of approximately 1.5 m above ground level at the side of the bridge between a busy street running parallel to the river and the Rhine promenade, each within a distance of 5–10 m. The distance to the river was about 20 m.

Measurements of aerosol and gas phase concentrations were performed continuously from 28 December 2004, until 4 January 2005. Due to the close proximity of the measurement site to the street a significant influence from local traffic on the measurements can be expected. During the New Years festivities large crowds of people gather along the Rhine promenade at and on the bridge to set off fireworks that typically start exactly at midnight. Therefore the measurement site was located in the center of Mainz and in the middle of the expected firework activity. It should be noted that additional fireworks are set off in other parts of the city and in neighboring towns and cities.

2.2. Instrumentation

Aerosol particle number concentrations were measured using a condensation particle counter (CPC, Grimm CPC 5.403) with a lower cut-off diameter of ~ 5 nm. This instrument measures particle concentrations up to 10^7 particles per cm^3 with a time resolution of 1 s.

The size resolved non refractory chemical composition of the sub-micron aerosol particles was measured with an Aerodyne time-of-flight aerosol mass spectrometer (TOF-AMS). The TOF-AMS generates a tightly focused aerosol beam into a vacuum chamber. The particles impact onto a heated surface (600 °C) where non-refractory aerosol components flash-evaporate and are ionized by electron impact. The ions are analyzed using a time-of-flight mass spectrometer with a calibrated detector. Particle size information is obtained by chopping the particle beam and applying a particle time-of-flight measurement. Mass concentrations of non-refractory aerosol components were calculated

from the ion signal intensity at the mass-to-charge ratios (m/z) of the ion fragments that are associated with the individual species. For this calculation the calibrated detector gain, the measured inlet flow rate and laboratory-measured relative ionization efficiencies (RIEs) for the individual species were used. A detailed description of the instrument and its operation can be found in [Drewnick et al. \(2005\)](#). During this project the TOF-AMS was set to measure aerosol mass concentrations and size information with a time resolution of 5 min.

Mixing ratios of organic trace gases such as methanol, acetone, benzene and toluene were measured with a time resolution of 1.5 min using a proton transfer reaction mass spectrometer (PTR-MS). In this instrument, H_3O^+ ions are generated in a hollow cathode from a plasma discharge. In a drift tube these ions undergo collisions with air and trace gas molecules. Molecules that have a higher proton affinity than water can be ionized by proton transfer reaction. These ions are analyzed in a quadrupole mass spectrometer and quantified using an ion detector. In this study we report measurements of m/z 33, 42, 59, 79 and 93, which have been attributed to methanol, acetonitrile, acetone, benzene and toluene, respectively. These identifications are in accordance with previous studies although minor contributions from other species, such as propanal to mass 59 cannot be ruled out ([Lindinger et al., 1998](#); [Williams et al., 2001](#)).

3. Results and discussion

3.1. Identification of fireworks components

Aerosol species mass concentrations are calculated from the TOF-AMS mass spectra by adding all fragments of the individual species, found at the various m/z . In order to extract the individual contributions from different species at a given mass to charge ratio m/z , a deconvolution algorithm is applied to the mass spectra ([Allan et al., 2004](#)). In addition to known isotope ratios and measured fragmentation patterns, this algorithm uses several assumptions concerning the assignments of certain m/z to individual species, which are based on the experience of aerosol measurements in the ambient atmosphere.

For the aerosol measurements during the fireworks event studied here, these assumptions may no longer be applicable since additional, more exotic species could be expected in the aerosol at

significant levels, causing a change in the assignment of individual m/z to certain species. Therefore in a first step of TOF-AMS data processing, the assignment of each m/z to possible species was examined. For each m/z from 5 to 120 individual time series of the signal measured over the whole measurement interval were plotted and possible elemental compositions were identified using information about species involved in fireworks chemistry. Relative signal intensity during and outside the time of the firework activities together with volatility information of the individual compounds relevant in fireworks chemistry resulted in a pretty robust overall picture of the assignment of the various m/z signals to individual species. Many of the potential firework generated species could be excluded, either because they are refractory and consequently could not be measured by the TOF-AMS, or because the time series of the particular m/z did not show any fireworks signature. A summary of m/z and related species that were found in the firework generated aerosol and that are different from the ‘standard’ TOF-AMS m/z -to-species assignments is shown in [Table 1](#).

Several of the m/z listed in [Table 1](#) are typically used to calculate the *total organics* mass concentration from the TOF-AMS mass spectra. To account for the different assignment of these m/z to other

Table 1
Unusual assignments of certain m/z in the aerosol mass spectra to individual species for the fireworks aerosol

m/z	Compound	Comment
7	Lithium	Weak but clear fireworks contribution
19	Fluorine	Weak but clear fireworks contribution
23	Sodium	Very intense fireworks contribution
24	NaH	Significant fireworks contribution
32	S (in addition to O_2)	Very intense fireworks contribution
36	H^{35}Cl	Very intense fireworks contribution
38	H^{37}Cl	Very intense fireworks contribution
39	^{39}K (mainly)	Extremely intense fireworks contribution
41	^{41}K , Organics	Very intense fireworks contribution
74	K^{35}Cl , Organics	Likely mainly KCl
76	K^{37}Cl , Organics	KCl and Organics

species during the measurement of the fireworks aerosol the deconvolution algorithm to calculate *total organics* from the measured mass spectra was adapted appropriately. For most of the additional species found in the firework generated aerosol the RIE (compared to the calibration species, ammonium nitrate) is not known, hence no absolute mass concentrations could be calculated for these compounds.

A similar procedure was performed for the trace gas species, measured with the PTR-MS. A time series for each of the species was plotted for the entire measurement interval and evaluated for potential fireworks influence. Time series for several of the species are shown in Fig. 1. For the aromatics measured with the PTR-MS, benzene, toluene, xylene and trimethylbenzene, no significant contribution from the fireworks was found in the data. All these species show similar diurnal patterns with some influence from local traffic, but without any strong influence from the fireworks. Only in the case of benzene there is a small firework related contribution, in the same scale as the regular diurnal variation caused by road traffic. A significant fireworks fingerprint was found for acetone, acetonitrile, and methanol. All these species have been reported previously as biomass burning emissions (Andreae and Merlet, 2001) and show a narrow, distinct peak during the time of the fireworks. With the exception of acetaldehyde all

these species do not show a very pronounced diurnal pattern. The diurnal pattern found for acetaldehyde agrees well with photochemical production processes, which are a typical source for this compound. One possible explanation for the absence of toluene and low mixing ratios of benzene from the firework signal (while other burning related compounds are present) is that the former are not efficiently produced when black powder is burned. Although the body of a firework is typically paper or cardboard (i.e. biomass) this part does not normally burn when the firework is set off. Plentiful evidence of unburned cardboard firework cases was seen the day after the fireworks all along the Rhine promenade.

3.2. Quantification of aerosol potassium

The mass concentration of each species, measured with the TOF-AMS is calculated by adding the individual contributions of the species to the mass spectrum (i.e. the fragment ions of the mother molecules – as determined in laboratory experiments) and conversion of this total ion current into a mass concentration. The calibrated MCP detector gives the number of ions collected for each of these m/z . The electron impact ionization efficiency (EI, calibrated with ammonium nitrate particles) and the RIE for the individual species (RIE, accounting for different ionization cross sections of different

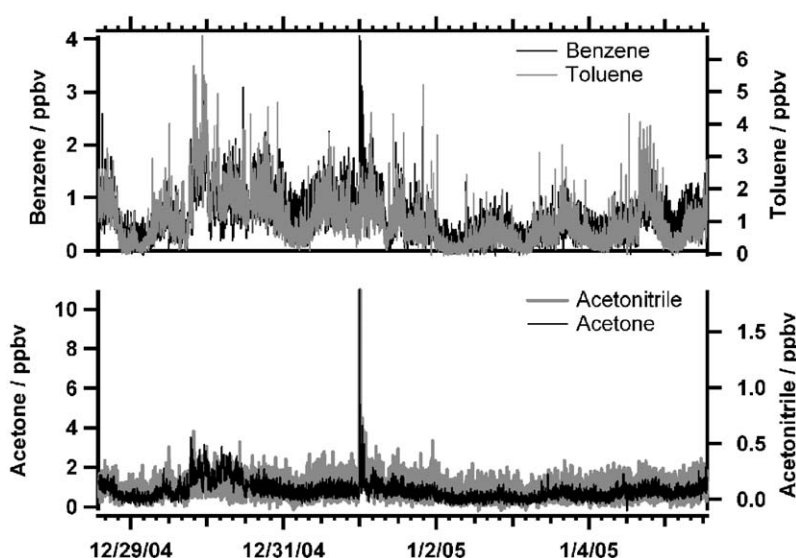


Fig. 1. Time series for a selection of the trace gases measured with the PTR-MS. In the upper panel two aromatics (benzene, toluene) are shown; in the lower panel time series for acetone and acetonitrile (usually used as a marker for biomass burning) are shown.

species, e.g. Hogrefe et al., 2004) allow to convert the number of ions detected with the MCP into the number of molecules arriving at the ionizer of the instrument. A collection efficiency factor (CE, determined in other field experiments) accounts for collection losses in the instrument due to bounce of particles from the vaporizer. In ambient aerosol measurements this factor has been found to be typically in the order of $CE = 0.5$ (Huffman et al., 2005) for the non-refractory species. Finally the number of molecules of a certain species that are entering the instrument per unit time are converted into an ambient mass concentration using the measured inlet flow rate of the TOF-AMS. A detailed description of these calculations can be found for example in Drewnick et al. (2004a) and Allan et al. (2004).

While aerosol potassium is not part of the suite of non-refractory species typically determined with the TOF-AMS, it is observed as contaminant in the instrument and the mass spectra are corrected for its contributions at m/z 39 and 41. Potassium is known to generate ions by thermal ionization on the hot vaporizer (surface ionization) with relatively high efficiency. However, since it is typically not quantified in ambient aerosol measurement with the TOF-AMS, no measurements of RIE of potassium in the aerosol exist so far.

Aerosol influenced by fireworks has a very different composition from typical ambient aerosol. In firework related aerosol potassium is one of the major components (Dutcher et al., 1999; Liu et al., 1997; Kulshrestha et al., 2004; Perry, 1999). A first approach to obtain a rough estimate of the RIE for aerosol potassium and consequently enable a quantitative measurement of potassium with the TOF-AMS was suggested by the analysis of a relatively undisturbed fireworks aerosol by Dutcher et al. (1999). Dutcher and coworkers used PIXE analysis to determine the elemental composition of an aerosol generated by fireworks in the Houston Astrodome during a baseball game and sampled with stacked filter unit samplers. Remarkably, they found an elemental concentration ratio of potassium to sulfur (2.76:1) that is virtually identical to the ratio of these elements in black powder, which is the major component of most fireworks. Black powder consists of 74% KNO_3 , 10.4% sulfur and 15.6% carbon (charcoal), resulting in a K/S mass ratio of 2.75. As one expects the largest fraction of the fireworks material to be converted into gas-phase compounds when burned, e.g. the major

fraction of sulfur should be oxidized to SO_2 , it may be just coincidental to find this agreement in the K/S ratios. Because nitrate was not detected in enhanced quantities in the fireworks aerosol (see below) it is also unlikely that the major fraction of the sampled aerosol consists of unburned fireworks material which conserves the original elemental composition. If we assume that during the Mainz' fireworks the sampled aerosol was dominated by firework generated material, and that during the fireworks the same K/S ratio of 2.76 as found by Dutcher et al. (1999) is present in our aerosol samples, we can use the measurement of aerosol S for a rough estimate of the aerosol potassium content. S is found in the aerosol mainly as sulfate or sulfuric acid, both summarized under TOF-AMS sulfate. The average sulfate concentration measured with the TOF-AMS in the fireworks-dominated aerosol (31/12/04 23:45–01/01/05 08:00) was $36.2 \mu\text{g m}^{-3}$, resulting in an average S concentration of $12.1 \mu\text{g m}^{-3}$. Assuming an average K/S ratio of 2.75 the average potassium concentration during this time interval is $33.2 \mu\text{g m}^{-3}$.

From the signal intensity at m/z 39 and 41 the so-called 'nitrate-equivalent' potassium concentration is calculated, which does not include a collection efficiency (CE) and RIE different from unity. The average nitrate-equivalent potassium concentration measured for the time interval given above is $48.1 \mu\text{g m}^{-3}$. If we assume an internal mixture of the firework aerosol components, we need to apply a CE factor of 0.5 (as for sulfate) and obtain as a result an average K concentration of $96.2 \mu\text{g m}^{-3}$. In order to derive a concentration of K of $33.2 \mu\text{g m}^{-3}$ in agreement with the K/S ratio reported by Dutcher et al. (1999), we have to assume a RIE of $RIE_K = 2.9$. Even though this RIE for potassium is subject to substantial uncertainty due to the assumptions made for its derivation, it is the first estimate for a RIE for TOF-AMS potassium measurements. Since no detailed information about the conditions and the components of the fireworks measured by Dutcher et al. (1999) are known, we do not know how similar the conditions of this fireworks with the one investigated here are. However, since this is the only available measurement on K/S ratios in ambient fireworks aerosol in the literature, we use this ratio to obtain a first approximation of the RIE of potassium and consequently to determine ambient aerosol potassium concentrations from our measurements.

3.3. Composition of the fireworks aerosol

Time series of the mass concentrations of the non-refractory aerosol species nitrate, sulfate, ammonium, total organics, chloride and potassium are shown in Fig. 2. Because of the large difference in ambient and firework aerosol intensity, the fireworks aerosol is cut off at $30 \mu\text{g m}^{-3}$ to make sure that the variations in ambient aerosol concentrations are still visible. Time series of the firework related aerosol, covering the whole intensity range, are shown below. It can be seen from Fig. 2 that the variation in ambient aerosol concentration is episodic rather than diurnal, and therefore probably rather associated with synoptic scale transport than with local emissions. The New Year's fireworks took place during an episode of relatively high aerosol

concentrations, which started around 29/12/04 18:30 and lasted until 02/01/05 03:00 (termed hereafter “background 1”). After this episode the particle concentrations decreased to very low values, and slowly increased again over the next few days (termed hereafter “background 2”). As “firework aerosol” we define the aerosol measured from 31/12/04 23:45 until 01/01/05 08:00 as described above.

Average mass concentrations of the non-refractory species measured with the TOF-AMS during the background periods #1 and #2 and of the firework related aerosol, as well as maximum concentrations during the firework aerosol are shown in Table 2. The composition of the sub-micron aerosol—as measured with the TOF-AMS—is shown in Fig. 3 for the background and the fireworks aerosol.

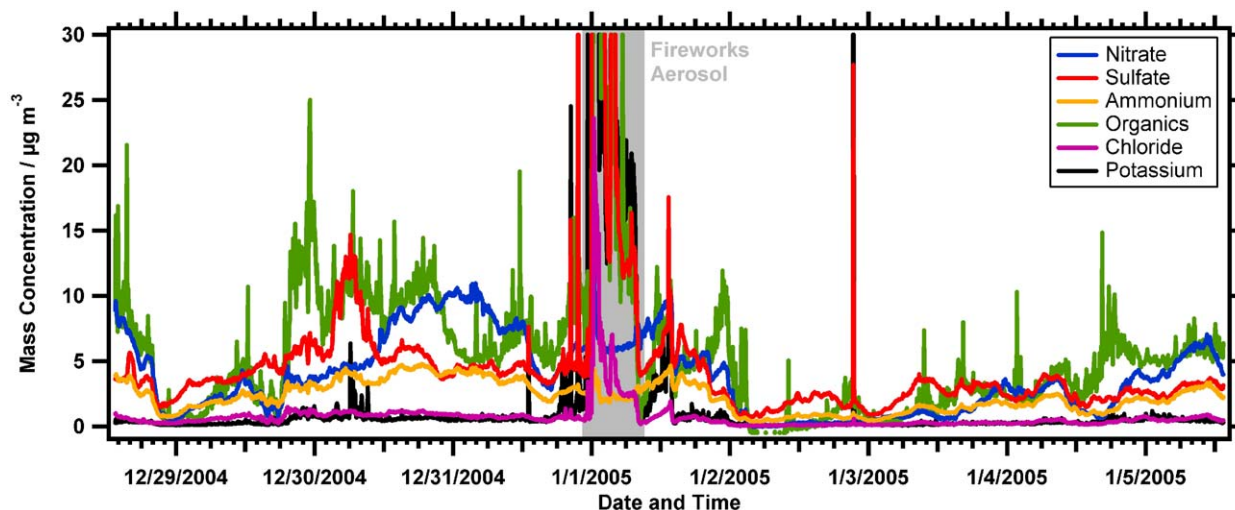


Fig. 2. Time series of the non-refractory aerosol components, measured with the TOF-AMS during the whole campaign. The firework generated aerosol is cut-off at $30 \mu\text{g m}^{-3}$ to make the variations of the ambient aerosol visible. The mass concentrations for the individual species for the time interval of the fireworks peak can be seen in Fig. 5 in more detail.

Table 2

Absolute and relative concentrations of the background and firework related aerosol as measured with the TOF-AMS

Species	Background 1	Background 2	Fireworks mean	Fireworks max
Nitrate	6.17 (25.1%)	1.94 (21.1%)	6.48 (5.8%)	12.63 (2.1%)
Sulfate	5.26 (21.4%)	2.43 (26.5%)	36.17 (32.5%)	209.03 (34.2%)
Ammonium	3.30 (13.5%)	1.42 (15.5%)	2.39 (2.1%)	4.32 (0.7%)
Chloride	0.78 (3.2%)	0.29 (3.2%)	5.13 (4.6%)	23.61 (3.9%)
Organics	7.86 (32.0%)	2.76 (30.0%)	28.03 (25.2%)	127.40 (20.8%)
Potassium	1.18 (4.8%)	0.34 (3.7%)	33.15 (29.8%)	234.12 (38.3%)
Total TOF-AMS	24.55 (100%)	9.18 (100%)	111.35 (100%)	611.11 (100%)

Given are the average concentrations for the background aerosol during the two aerosol episodes as defined in the text and for the fireworks aerosol. In addition maximum concentrations during the fireworks are shown. Absolute concentrations are given in $\mu\text{g m}^{-3}$.

As shown in Table 2 and Fig. 3 the aerosol mass concentrations during background interval #2 are only about one-third of the concentrations during the first background time period. However, the relative composition of both aerosols is very similar. During the fireworks and especially in the period of maximum firework intensity, not only most of the aerosol mass concentrations are much higher than during the background measurements, but also the relative composition of the aerosol is very different from the background composition, highlighting the

main contributors from the fireworks. From Table 2 it is very obvious that neither aerosol phase nitrate nor ammonium is generated in the fireworks in significant amounts. For both species the average mass concentrations are similar during the fireworks and the corresponding background (#1) interval. Especially the complete absence of an increase in nitrate concentration is remarkable since nitrates are a major component of fireworks. Apparently all the nitrates in fireworks are quantitatively converted into NO_x , which has been found previously to

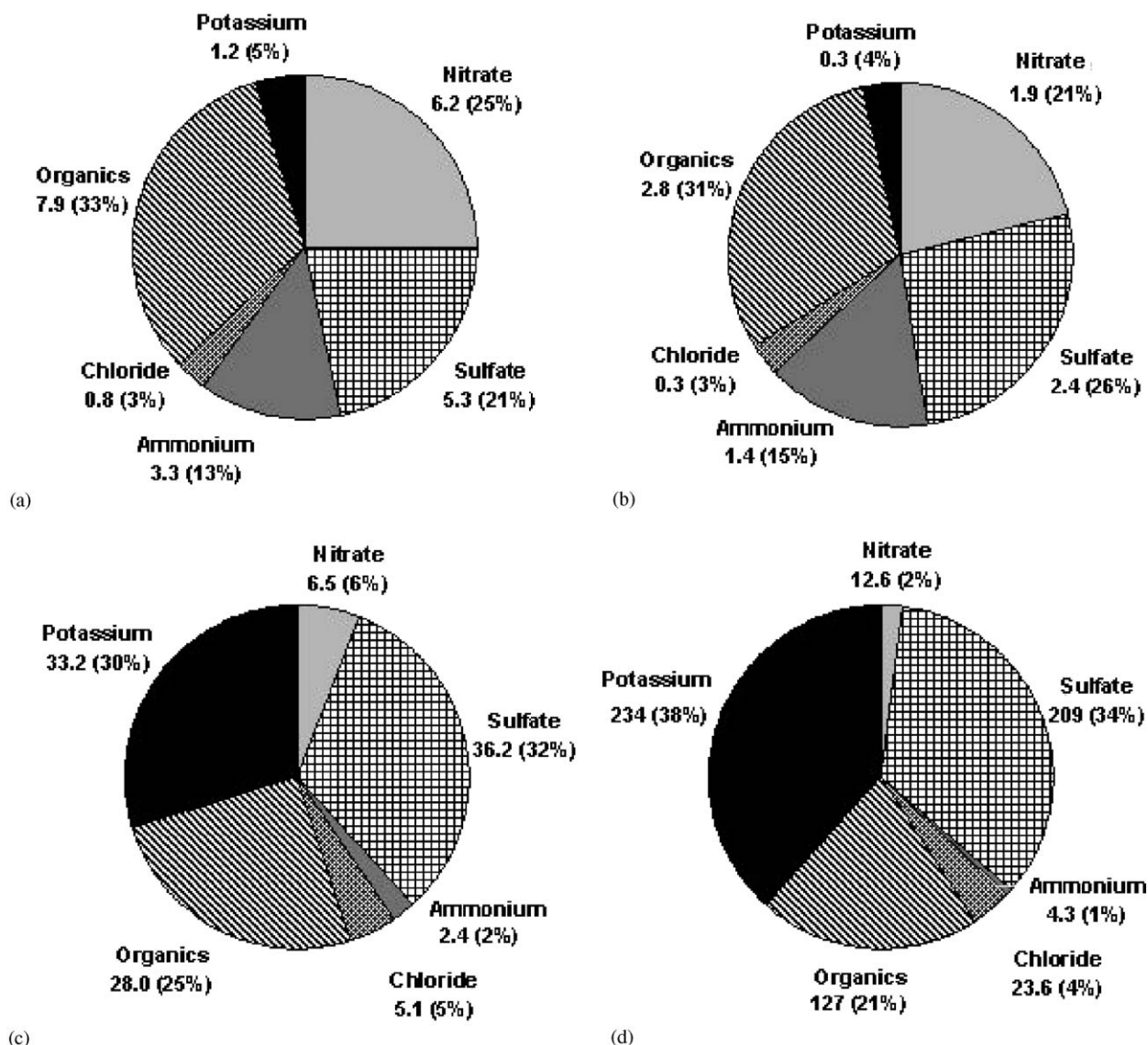


Fig. 3. Composition of the sub-micron aerosol as measured with the TOF-AMS (non-refractory species only) during background periods #1 (a) and #2 (b) and during the fireworks aerosol (c). Also the composition of the aerosol during the maximum concentrations in the fireworks is shown (d). Absolute concentrations are given in $\mu\text{g m}^{-3}$.

increase during fireworks (Mandal et al., 1997; Wehner et al., 2000; Ravindra et al., 2003).

The most intensive contributions of the fireworks to the aerosol composition are seen in sulfate, total organics and potassium, resulting in large increases in the mass concentrations of these species. For sulfate a sevenfold increase of the mean fireworks concentration over background (#1) and a 40-fold increase are observed at the maximum. For organics the increases are 3.5 times (mean), and 16-fold (max), respectively. For potassium the largest increase is found with a 28-fold increase for the average concentration of the fireworks and a 200-fold increase for the maximum concentration. If one takes into account that the averages of the potassium background concentrations are increased by approximately a factor of two by a few K-peaks (see Fig. 2)—very likely due to scattered fireworks explosions outside the actual fireworks event – these increases for potassium are even larger, showing the low abundance of this element in regular ambient aerosol.

Interestingly, even though the absolute concentrations of chloride in the fireworks aerosol are relatively low the increase in chloride concentration is similar to the sulfate increase with an almost 7-fold increase for the mean concentration and a 30-fold increase in the maximum of the chloride concentration.

A closer look at the average fireworks and background aerosol mass spectra and the time series for the individual m/z signals gives more insight into the composition of the organic aerosol. Since a large variety of organic compounds are vaporized and ionized together and undergo significant fragmentation during these processes, it is not possible to extract mass concentrations for individual organic species in the aerosol from the mass spectra. Thus the total organics signal is given here as the sum of all ion signals, resulting from the fragmentation of all organic molecules. These signals are identified as those signals that were not associated with the fragmentation of any of the inorganic species. However, investigations of the organic aerosol fraction have shown that the total organics can be separated into two components: hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA, Zhang et al., 2005), that together make up most of the measured organics signal. Mass spectra of HOA show high similarity to those of freshly emitted traffic aerosols while spectra of OOA closely resemble those of aged

organic aerosols. The major peaks in both subsets of the organic aerosol mass spectrum can be used as tracers for both types: m/z 44 (mostly CO_2^+) for OOA and m/z 57 (mostly C_4H_9^+) for HOA. Time series of the individual m/z signals show that those associated with HOA do not show significant contributions to the fireworks aerosol, while those associated with OOA show a large fireworks peak. Apparently HOA, similar to that found in traffic-related aerosols, is not generated in the fireworks, while the major part of the increased total organics during the fireworks aerosol (see Table 2 and Figs. 2 and 3) is mainly due to oxidized organic species. On the other hand, a distinct diurnal pattern is found for the HOA-related m/z that reflects the diurnal traffic pattern at the site outside the time of the fireworks, while no significant diurnal pattern is found for m/z related to OOA. As an example of the differences in these organic aerosol components in Fig. 4, size distributions for m/z 44 (marker for OOA) and m/z 57 (marker for HOA) are shown for the fireworks aerosol. The differences in the size distribution of these two aerosol components are very distinct. The (likely) traffic-related HOA aerosol has a bimodal distribution with a small particle mode around 70 nm and extending down to a few tens of nm and an accumulation mode around 250 nm, similar to organics size distributions found in New York City (Drewnick et al., 2004b). Since both modes of this size distributions are relatively broad, the small particle mode for m/z 57 appears more as a shoulder on the small particle size of the accumulation mode. The size distribution for the OOA marker is monomodal with a mode diameter around 400 nm, very similar to the size distributions measured for sulfate and chloride measured during the fireworks (not shown).

Total aerosol mass concentrations of more than $600 \mu\text{g m}^{-3}$ during the peak of the fireworks aerosol concentration may cause adverse health effects to susceptible persons. However, due to the short exposure duration to these peak concentrations (~ 15 min) these effects will be limited. The average total mass concentration measured with the TOF-AMS during the whole day of 1 January was $51 \mu\text{g m}^{-3}$, which was above the EU particle standard according to the *EU Framework Directive on Ambient Air Quality* for PM_{10} : $50 \mu\text{g m}^{-3}$, which is not to be exceeded more than 35 days per year. It should be noted that the aerosol measured with the TOF-AMS is not only limited to non-refractory aerosol components, but also to particle sizes below

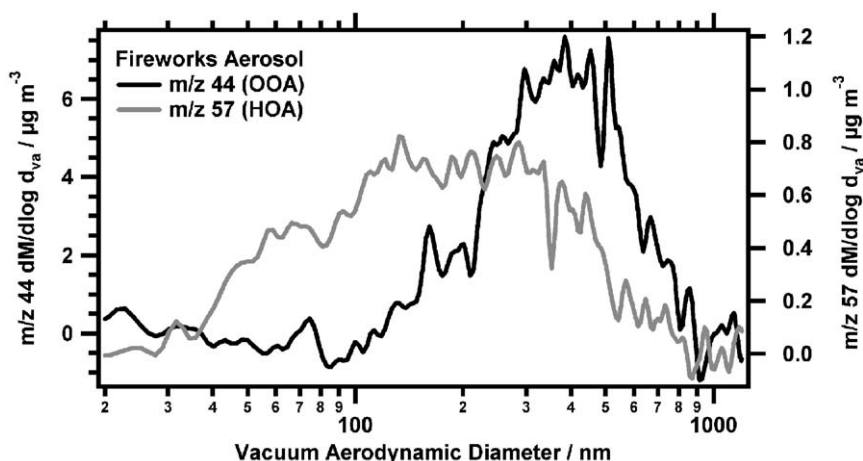


Fig. 4. Average size distributions for m/z 44 and m/z 57 during the fireworks aerosol. m/z 44 is a marker for oxygenated organic aerosol (OOA), m/z 57 is a marker for hydrocarbon-like organic aerosol (HOA).

$\sim 1 \mu\text{m}$ ($\text{PM}_{1.0}$). This means that the regulated PM_{10} concentration during this day was likely much larger than the concentration measured with the TOF-AMS.

3.4. Temporal evolution of the fireworks composition

For evaluation of the temporal evolution of the fireworks composition the time series of some trace gas constituents (acetonitrile and acetone), of several aerosol species (sulfate, total organics, potassium, and chloride) and the time series of particle, number concentrations are shown in Fig. 5 for the time interval of the fireworks aerosol. For all trace gas and aerosol species as well as for the particle number concentration a sharp increase in concentration is observed exactly at midnight, when traditionally the fireworks begin. It is peculiar that for all these aerosol concentrations and trace gas mixing ratios, a short depression was found that starts a few minutes after midnight and lasts about 10–15 min. After this depression all concentrations start rising again and reach within several minutes the maximum concentrations observed during the fireworks. We assume that the sharp increase in concentrations just after midnight is due to the firing-off of a large number of fireworks exactly at midnight. After this initial peak particle concentrations fall off for a short period of time, perhaps when people pause to exchange wishes or to toast the onset of the New Year. Accordingly we have called this short depression in concentrations the “champagne dip”. After well-wishing the fireworks

resume for a prolonged period, generating the largest concentrations observed during the whole firework time. After reaching their peak concentrations around 00:20–00:25 aerosol concentrations decay gradually within the following hours until they reach approximately pre-fireworks levels around 08:00 in the morning.

It is interesting that while all aerosol species concentrations, as well as the aerosol number concentrations (5-min average) track each other fairly well, the trace gas concentrations show a somewhat different temporal evolution. While the aerosol concentrations peak about 20–25 min after midnight the peak concentrations of the trace gas compounds are found approximately at 00:50. This might be an indication that the trace gas species measured with the PTR-MS are generated only after some delay after the explosion of the fireworks.

As shown in Fig. 5 the CPC measurements were performed with a time resolution much better than 5 min. While the 5-min averages of the particle number concentration agrees reasonably well with the trends of the 5-min averages of the species mass concentrations, measured with the TOF-AMS, the 15-sec data show some additional features. Especially at midnight, when the sharp increase in aerosol and trace gas concentrations was observed, huge particle number concentrations were measured for a very short time interval, reaching almost $500\,000 \text{ cm}^{-3}$ (the maximum of the peak is cut off in Fig. 5). In the 5-min averages this peak is somewhat leveled out. It is possible that this huge concentration is caused by a single cracker or sparkler

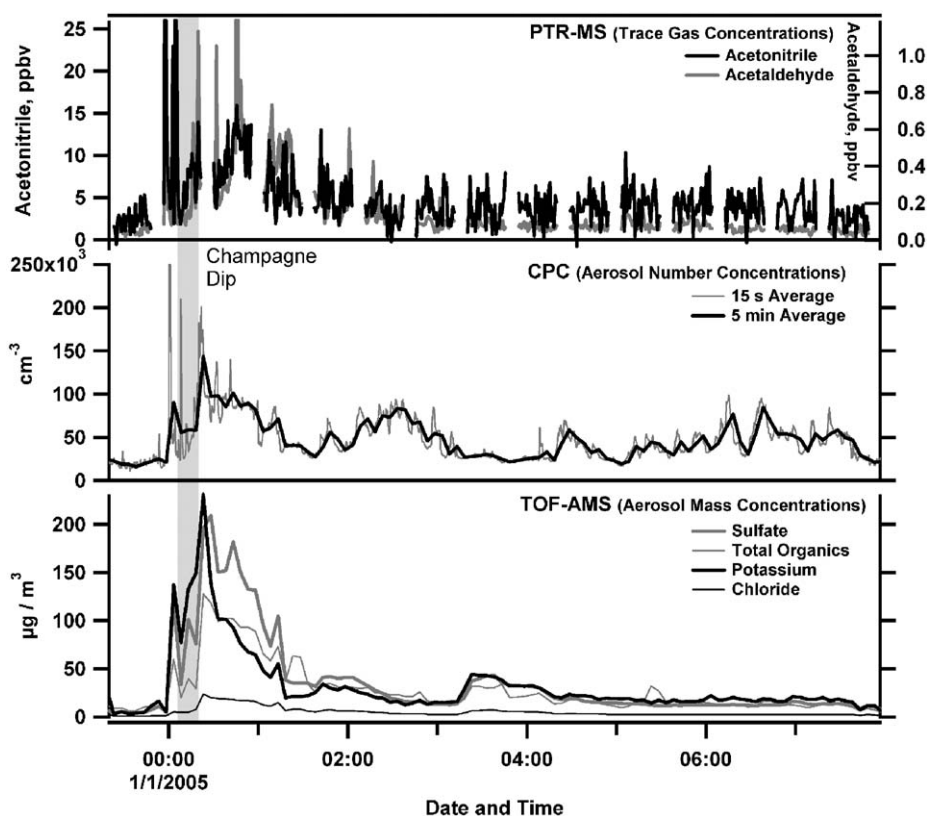


Fig. 5. Time series of trace gas volume mixing ratios, aerosol particle number concentrations and aerosol species mass concentrations for the fireworks time interval. The marked time interval is the “champagne dip”.

exploding very close to the aerosol and gas phase inlets. However, we do not believe that the whole peak just after midnight is caused just by this single event since no other events like this are observed during the remaining time of the fireworks and after the event a large amount of firework debris and remnants was found in the immediate vicinity of the inlets. Also changes in meteorological conditions are less likely to be the cause of the “champagne dip”. The wind speed was very low during the whole time of the fireworks, with average wind velocities around 0.6 m s^{-1} . The wind direction changed between southerly and northern directions, mostly advecting air parcels from along the Rhine promenade that could approximately be regarded as a linear source of fireworks aerosol. Nevertheless, changes in the advection and dilution of the air may have caused the “champagne dip” pattern as well.

4. Conclusions

The time-of-flight aerosol mass spectrometer (TOF-AMS), a condensation particle counter

(CPC) and a proton transfer reaction mass spectrometer (PTR-MS) were successfully deployed at a site close to the Rhine river in Mainz, Germany, in the center of firework activities over the 2004/2005 New Year’s festivities. For the TOF-AMS the data processing routines had to be adjusted to the changed composition of the fireworks aerosol, compared to regular ambient aerosol. Using a relationship between sulfur and potassium concentrations in a fireworks aerosol, found in the literature, it was for the first time possible to estimate the relative ionization efficiency for aerosol potassium, as measured with the TOF-AMS. With this procedure we found an RIE of 2.9 for potassium.

Several organic trace gases were measured during this project. While the aromatic compounds did not show any significant contribution from the fireworks emissions (e.g. toluene), other species, which are related to burning or biomass burning processes showed significant increases during the fireworks (e.g. methanol and acetone). In the aerosol a significant increase in particle number concentration

as well as in the mass concentration of several species was found. The main non-refractory aerosol components of the fireworks were potassium, sulfate and organics with peak mass concentrations of 230, 210 and 130 $\mu\text{g m}^{-3}$, respectively. Chloride mass concentrations were significantly lower with maximum concentrations of 24 $\mu\text{g m}^{-3}$, but also for this species the increase compared to the ambient background concentration was 30-fold. As a consequence of these enormous concentrations of soluble aerosol material a significant influence on the cloud condensation nuclei (CCN) population has to be expected for fireworks affected aerosol.

It was possible to separate the measured total organics signal into two contributors: hydrocarbon-like organic aerosol (HOA) that is mainly related to fresh traffic exhaust and oxygenated organic aerosol (OOA) that is composed of more oxidized organic material. While for HOA no significant contribution from the fireworks was found, OOA produced most of the large organics concentrations measured during this event. For 1 January, the average total aerosol mass concentration at the site exceeded the EU particle standard for air quality of 50 $\mu\text{g m}^{-3}$ not to be exceeded for more than 35 days per year.

The temporal evolution of the fireworks composition showed a sharp increase in all measured concentrations just after midnight, followed by a short depression of several minutes, which we call the “champagne dip”. After this interval of lower concentrations the largest aerosol and trace gas concentrations were observed with a maximum for the aerosol concentrations around 00:20 and a maximum of the trace gases about half an hour later.

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