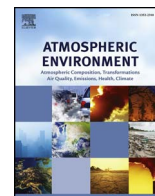




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Visibility in the Netherlands during New Year's fireworks: The role of soot and salty aerosol products

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ABSTRACT

The visibility on New Year's nights in the Netherlands is low during stagnant weather. This is due to the scattering and absorption of light by the aerosol-smoke from the fireworks. We made an assessment of the responsible aerosol-species. The investigation took place during the New Year's night of 2009. Measurements were made at a regional site in the centre of the country away from specific local sources. An Integrating Nephelometer measured the light-scattering by the inherent compounds after removal of water from the aerosol by drying the air. The actual light-scattering was determined in an open-air scatterometer; it was a factor of five higher than the “dry” value. The difference in actual and “dry” light-scattering can only be explained by water-uptake of the salty hygroscopic components of the aerosol. This hypothesis is substantiated by measurements of the composition of the aerosol. The size-dependent concentrations of the salty ionic species were determined on-line with a MARGA-“sizer”. These components were for a large part in particles in the size range that most effectively scatter light. The “dry” light-scattering was exerted by the inorganic salt components and the sooty carbonaceous material alike. However, the salty products from the fireworks are hygroscopic and take up water at the high relative humidities occurring that night. This explains the fivefold larger light-scattering by the wet ambient aerosol as compared to that by the dry aerosol in the integrating nephelometer. The visibility, which is the inverse of the open-air scattering, is thus indirectly governed by the salty products of the fireworks due to their uptake of water. Under stagnant weather conditions during New Year's nights in the Netherlands both the aerosol concentrations and the relative humidity are high; this implies that the ionic species govern the low visibilities in general, be it via their uptake of water.

1. Introduction

The fireworks during New Year's night in the Netherlands are rather unique because a better part is ignited in the streets. This gives rise to high concentrations of aerosol-smoke at street level and especially during stagnant weather this is accompanied by low visibilities. The visibility is reduced by the scattering and absorption of visible light. The present study was a sequel to an investigation in the previous year which showed that half of the aerosol consisted of sooty material with the rest inorganic salts (ten Brink et al., 2017).

The visibility may not be affected in the same way by the mentioned two types of compounds, because the scattering is very sensitive to the size of the particles. Furthermore the salts are hygroscopic and could take up water by which the aerosol particles grow in size and scatter more light. We investigated this hypothesis by assessing the relation between the size/composition of the aerosol and the visibility; this

relation is briefly introduced in the next subsection. The light-absorption by the soot was independently tested.

1.1. Visibility, light-scattering and hygroscopic growth

The visibility is defined as the maximum distance at which objects are discernible; it is known as visual range in aviation. The visual range is reduced because aerosol particles scatter the light on its way from the object to the observer. This distance is less at higher aerosol concentrations. Originally the visibility was determined with a long-path transmissometer and the light-reduction measured was extrapolated to the distance at which the light intensity would decrease to a few percent of the original value. Nowadays another method is used. The light scattered by the aerosol is measured with a scatterometer. The scattering is quantified via the light-scattering coefficient, which is a measure for the relative decrease in intensity of the light per meter. Its

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unit is m^{-1} . The relation between visibility and measured light-scattering (coefficient) is standardised (KNMI, 2005) via the following inverse relation:

$$\text{Vis} = 3.0 / b_{\text{scat}} \quad (1)$$

with visibility (Vis) in meters and the light-scattering coefficient (b_{scat}) in the unit m^{-1} . In the manual the Meteorological Optical Range is the official term for the visibility.

Equation (1) is described in detail in the classical textbook on aerosol science “Smoke, dust and haze” (Friedlander, 2000). There a full chapter is devoted to the light-scattering by aerosol particles; the book also describes the approach of assessing the contribution by the various aerosol compounds to the light-scattering. First, the light-scattering coefficient is determined in a so-called integrating nephelometer. Integrating means that all scattered light is collected and not at a given angle for which the signal is a complex function of particle size. Before the air arrives in the measuring section of the instrument it is heated to remove the water from the aerosol. The reason is that the aerosol-water would otherwise contribute to the light-scattering, while its concentration is not determined.

Graphs in textbooks (e.g., Hidy, 1984) provide the values for the scattering coefficient as a function of mass at a given aerosol size. The following feature is also explained there. A rather steep maximum occurs at a particle size that corresponds to the wavelength of light, which for visible light is around a diameter of $0.50 \mu\text{m}$. When compounds are preferentially present in aerosol of this size they contribute most to the light-scattering. This is the reason that we specifically measured the mass concentration of the compounds in the size range of $0.2\text{--}2 \mu\text{m}$. This approach was also followed in an earlier study to assess the contribution of the major components of ambient aerosol to the light-scattering (ten Brink et al., 1997). To put this in further perspective: a $\text{PM}_{2.5}$ mass concentration of $23 \mu\text{g m}^{-3}$ corresponded to a light-scattering coefficient of $1.0 \times 10^{-4} \text{m}^{-1}$ (ten Brink et al., 1996).

The actual light-scattering in the atmosphere is exerted by particles that contain water. This water is taken up by hygroscopic inorganic salt compounds like ammonium nitrate, even at a moderate relative humidity of 60%. The water uptake by the hygroscopic compounds of ambient aerosol and its effect on the light-scattering has been studied in a special set-up in our laboratory in which the relative humidity can be varied (ten Brink et al., 2000; Veeffkind et al., 1996). The average increase in light-scattering was a factor of two at an RH of 85%. Also the decrease in light-scattering when the air is dried was assessed (Dogle et al., 1998). This combined expertise was used in the evaluation of the present measurements.

The mass concentrations of the hygroscopic ionic compounds were determined as a function of size with the automated on-line MARGA-“sizer” (ten Brink et al., 2007). The size classification is discussed in the next section. The operating principle of the MARGA itself is summarised here. At the inlet steam is injected into the sampling air. This condenses onto the aerosol particles that grow to droplets, which are subsequently collected in a cyclone. The soluble fraction of the compounds dissolves in the water. The drain from the cyclone is fed to an ion-chromatograph for direct on-line chemical analysis of the dissolved ions. An important aspect is that the method representatively collects the semi-volatile ammonium nitrate. This is important because its concentration was high and it strongly contributes to the light-scattering at the measuring site. This contribution has to be subtracted from the total light-scattering to obtain the light-scattering exerted by the aerosol from the fireworks.

2. Experimental

2.1. Campaign

The measuring campaign was part of a project to assess the size and

composition of the aerosol in the Netherlands in a number of months in the year 2008. The study was extended for an extra day for the present investigation of the aerosol during New Year's night of 2009. The measurements were performed in the CESAR-observatory at Cabauw in the centre of the Netherlands, between the cities of Utrecht and Rotterdam. The aerosol at the site originates from a mix of fireworks, instead of being from a specific type of fire-crackers at a street location. Furthermore visibility data were available.

Fog was forecast for New Year's night, but did not develop. The weather was stagnant though with a light wind from a north to easterly direction with velocities in the class of 1m s^{-1} . These and other hourly data, including those on relative humidity (RH) and visibility, were obtained from the standard instrumentation of which the data are given in tables of the national network (KNMI, 2009) for the site.

Note. The RH that night was in excess of 95%. With an uncertainty in hygrometers of 5%, this means that the actual value can be anywhere between 95% and 100%. The associated extra light-scattering by water taken up by hygroscopic components of the aerosol has an uncertainty of more than an order of magnitude. Reversely, the larger value of the open-air light-scattering measured as compared to the “dry” light-scattering is a better measure. The five-fold increase found in section 3.1 is due to the uptake of water by the hygroscopic particles and occurs when the RH is 97–98%. This uncertainty is substantially less than that of the tabulated RH.

2.2. Instrumentation

2.2.1. Light-scattering and visibility

An Integrating Nephelometer (TSI 3563) was used to measure the aerosol light-scattering. In this instrument the sampling air is dried by a heated inlet to a reference low relative humidity of 40%; at this humidity the water content is negligible and the aerosol is called “dry” (ten Brink et al., 2000). The Integrating Nephelometer was located on a measuring platform at a height of 60 m. This means that the aerosol as encountered there is not of a local origin and thus representative for an average more regional aerosol. The instrument provides data with a 5 min resolution, with zeroing occurring every tenth time-step.

Values for the directly measured visibility were obtained from the data tabulation of the national meteorological network (KNMI, 2009); it is termed visual range in that database. The data are the average and maximum and minimum values in an hourly interval. The visibility is derived from an open-air light-scattering instrument (KNMI, 2005).

2.2.2. Composition as a function of size; the MARGA-sizer

Measurements of the concentration of the major ions were made with the MARGA-sizer. This instrument was located inside the meteorological tower of the CESAR site at Cabauw. Due to space restrictions the instrument needed a long sampling line. The advantage was that the air in the line is warmed up and that the aerosol is dried and thus size-classified in the dry state.

The MARGA-sizer measures the ionic components as a function of size and has been described before in detail with regards to monitoring of the standard inorganic species in the Netherlands, viz. nitrate, sulphate, ammonium (ten Brink et al., 2009; ten Brink et al., 2007). Its long-term performance was compared with that of a standard Aerodyne Aerosol Mass Spectrometer at the site (Mensah et al., 2012). We will summarise the main characteristics of the size-classification of the MARGA-sizer because of its importance for the light-scattering. Furthermore the novel detection of the cations is discussed.

The size-classification occurs via a set of parallel impactors. The impactors have cut-off diameters of 2.0, 0.1, 0.56, 0.32 and $0.18 \mu\text{m}$. Aerosol particles behind these impactors have diameters smaller than these respective values. A total cycle of sampling and analysis takes 2 h. The characteristics of the impactors were checked after the campaign in the lab. The measured cut-off diameters of the impactors were close to the factory value. However, a constant fraction of around 7% of the

particles larger than the cut-off size was transmitted. The correction for this artifact is of minor importance, because the maximum of the mass concentration occurred at the size range which contributes most to the light scattering. The mass concentration of ions in the next size range was less and scattering by these particles is also less efficient which makes the interference negligible compared to other uncertainties in the measurements as discussed below.

Cations, like potassium and magnesium, were present in high concentrations during the fireworks. It was the first time that these were measured with the instrument and a complication in their measurement was noticed. It appeared to be connected with the analysis system. The detection of the ions occurs in the drain of the collector of the aerosol. This is a cyclone that collects the droplets that have grown on the aerosol particles in the air-sampling line by injection and condensation of steam. The drain from the cyclone is split in half and part of the flow is led to a pre-concentrator column on which the cations are collected. In the subsequent analysis step they are carried off in a much smaller flow of water with a corresponding increase in concentration and increase in detection sensitivity.

Instrument blank values come from an extra parallel sampling channel in which a filter removes all aerosol. Sampling through this line is repeated and the value in the second blank run is used as the “field” blank. It is obtained in every measuring cycle and subtracted from the values measured in the aerosol channels. The lower Limit of Detection, as given by the values during the rest of the months, compares very favourably with their concentrations found in the aerosol during the fireworks.

The complication in the detection is the presence of substantial quantities of potassium and magnesium in the blank channel during the fireworks. Analysis of the blank channel follows the measurement of the channel with the impactor with the highest cut-off diameter and thus the largest amount of material. The artifact is apparently due to hold-up and subsequent slow release of sample on the preconcentrator-column. The average carry-over to the next channel for potassium is 9%. This was corrected for in the way described in the Appendix.

The carry-over is more severe for magnesium, with significant concentrations in the second consecutive blank. Details are given in the Appendix, where it is shown that the hold-up is so severe of that only the Mg-concentration in the 2.0 μm channel can be reliably corrected for. A total concentration of Mg in the submicron aerosol at the peak of the fireworks aerosol of 4 $\mu\text{g m}^{-3}$ was thus estimated. This is a relatively small value compared to that of the other ions and its uncertainty thus seems of lesser interest. However because magnesium is divalent and has a low atomic number its ion equivalent value is four times that of potassium and it therefore is significant as ionic compound. Magnesium data in the other channels are calculated with the potassium concentration as the reference, assuming that ratio of the two components is equal to that in the 2.0 μm channel.

2.2.3. Black Carbon and light absorption

A MAAP was present with which Black Carbon concentrations were measured. From the MAAP data the light absorption by the aerosol was derived. This absorption contributed to the reduction of the visibility. The light absorption by this component was derived from the values of the Black Carbon concentration and used for an estimate of the contribution of the light absorption to the light extinction and visibility. In addition the concentration of Elemental Carbon derived from the Black Carbon data was used to make an estimate of the concentration of total carbon, as discussed in section 3.2.

3. Results and discussion

3.1. Light-scattering and visibility

An Integrating Nephelometer was used to measure the light-scattering after drying the air and aerosol in the heated inlet. The relative

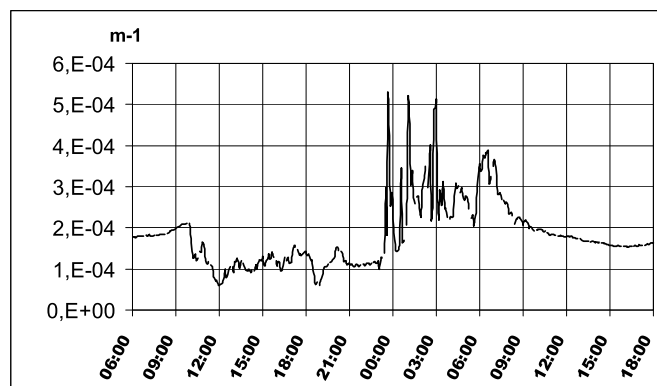


Fig. 1. The dry aerosol light-scattering coefficient at 550 nm as a function of time at the 60 m platform of the CESAR-observatory at Cabauw during New Year and New Year's eve 2009.

humidity thereby decreases to values of about 40% at which value the amount of water is small relative to that of the inherent aerosol components (ten Brink et al., 2000). The results of the monitoring of the light-scattering as a function of time are presented in Fig. 1. The graph is illustrative for the rapid changes that were even encountered at this rural site at a height of 60 m. For instance, there are peaks in the light-scattering just before midnight and at 1:00 a.m. with a duration of at most 5 min, which is the time resolution of the instrument.

A peak with a longer duration started around 3:00 a.m. and it is this period that we use for evaluation. The aerosol at that time is representative for the average regional aerosol. In this respect we like to mention that the aerosol observed at the 60 m platform shortly before midnight was not noticed by the MARGA-sizer at ground-level; it was thus most likely from high-flying local rockets. The light-scattering during the peak concentration of the advected aerosol at 3:00 a.m. was around $5.0 \times 10^{-4} \text{ m}^{-1}$.

The visibility at this time was 1000–1400 m (KNMI, 2009). We translated the visibility back to the actually measured light-scattering by the scatterometer, with the use of equation (1) in section 1.1. The actual ambient light-scattering coefficient was thus in the order of $25 \times 10^{-4} \text{ m}^{-1}$, which is five times higher than the “dry” light-scattering. This large difference between the measured open-air and “dry” light-scattering can only be explained by uptake of a large amount of water by the salty hygroscopic components of the aerosol, as discussed next.

3.2. Composition and size of the aerosol

The composition as a function of size was measured with the MARGA-sizer, discussed in section 2.2.2. The results are depicted in Fig. 2; it shows the concentration of the major ions in the aerosol as a function of size during New Year's Eve and night. The compound potassium was the best tracer for the aerosol from the fireworks. The maximum value for potassium occurred 3 h after midnight with a secondary maximum at 6:00 a.m. The submicron inorganic aerosol contained, in addition to potassium, sulphate and chloride (ions) and some magnesium. The concentrations of chloride and magnesium are not shown because these followed that of potassium. The concentration of chloride was 60% of that of potassium; for magnesium it was about 15%.

The concentrations of two other ions, nitrate and ammonium were also high, but these did not show peaks during the night and the species were therefore not produced in the fireworks, but are part of the background aerosol. The concentration of ammonium is not shown in Fig. 2, but its value was close to half of that of nitrate.

The ratios of the major components were first compared to those determined the previous year (ten Brink et al., 2017), at an urban

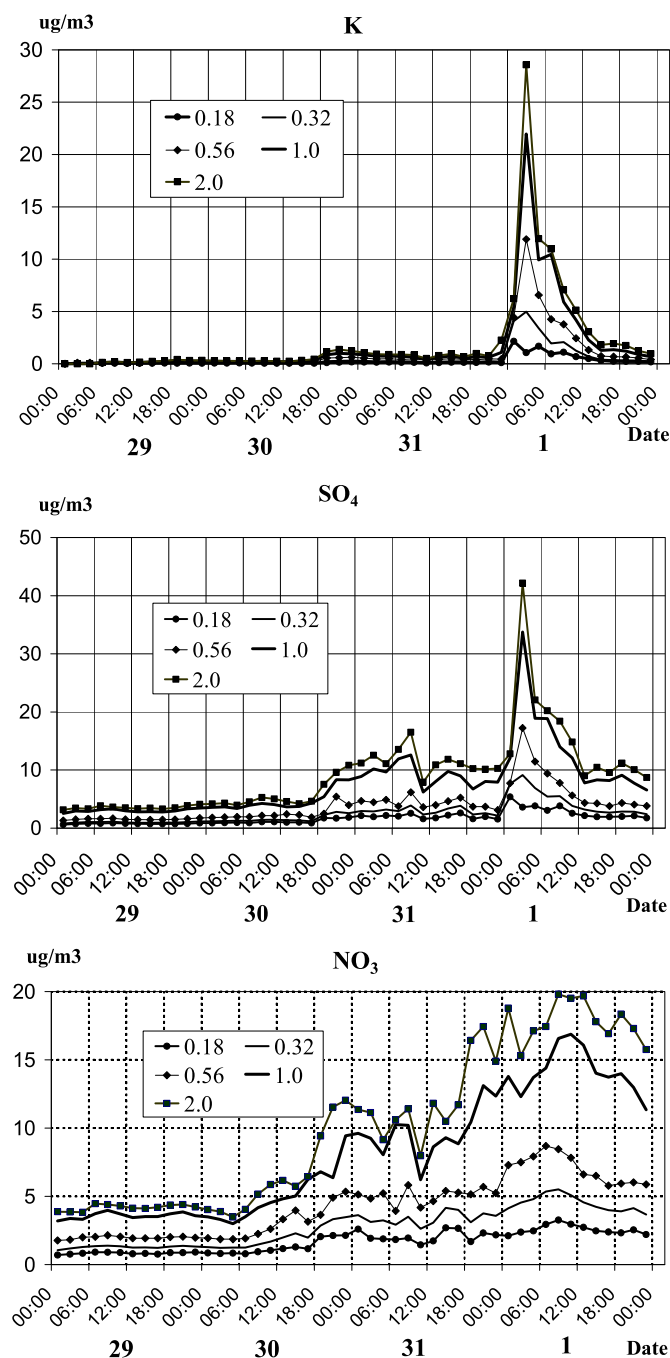


Fig. 2. Time series of the concentration of potassium, sulphate and nitrate in aerosol that is smaller than the indicated cut-off diameter in μm . Measurements made at the surface level of the CESAR-observatory in the same time period as mentioned in Fig. 1. Note the different scales.

background site in the town of Schiedam near Rotterdam. The ratio of potassium to chloride is similar at both sites. This also applied for magnesium, but assessing its concentration was rather complex, as discussed in the appendix. The concentration of sulphate is elevated during the time that the plume of the fireworks aerosol passes the measuring site but it is present in the background aerosol, as seen in Fig. 2. The background value was subtracted with the use of nitrate as a reference. The ratio of the fireworks-sulphate to potassium was then found to be very similar to that measured the year before.

It appears from the above that the ionic composition of the aerosol from the fireworks in the Netherlands is very constant. A first inference then is that the contribution of the sooty carbonaceous material to the

aerosol mass is also similar to that at the urban site, where it contributed 40% to the mass. We use the term “carbon” in the mentioned reference (ten Brink et al., 2017).

The mass concentration of the ions, including that of the background aerosol, had its maximum in the size range $0.3\text{--}1.0\ \mu\text{m}$ (Fig. 2). The concentration in that range can be obtained by subtracting the values of the two solid lines in the figures. It is the size-range which, on a mass basis, most effectively scatters visible light, as discussed in section 1.1.

The only component of which the mass-concentration as a function of size was not measured was carbon. An estimate of its total concentration was given above. An independent estimate was made via the concentration of Black Carbon and a conversion factor to extrapolate this value. The concentration of “carbon” should be around $80\ \mu\text{g m}^{-3}$. Part of this “carbon” is from background aerosol, with a contribution of $25\ \mu\text{g m}^{-3}$ as deduced from the Black Carbon concentration in the periods with an absence of fireworks aerosol. The contribution of “carbon” to the light-scattering is discussed in the next section.

3.3. Aerosol composition and light-scattering/visibility

A first observation is that all major inorganic ionic species have a highly similar size distribution, see Fig. 2. This also applies to the background aerosol species ammonium nitrate. It implies that they contribute according to their mass concentration. An estimate was made of the total contribution of the ionic species to the dry light-scattering. The measured concentrations as a function of size were multiplied by the light-scattering value per mass unit at that size, as discussed section 1.1.

The calculated light-scattering coefficient amounts to $3.3 \times 10^{-4}\ \text{m}^{-1}$ with an uncertainty of 20%. This uncertainty is mostly due to the rather coarse size-classification (ten Brink et al., 1997). After subtraction of the contribution by the background aerosol the light-scattering by the salty products of the fireworks would amount to $2.6 \times 10^{-4}\ \text{m}^{-1}$, which is about half of the measured value. Given the uncertainty in this value we can not exclude that the contribution of the “carbon” to the dry light-scattering is equally high. This is possible when the carbon would be concentrated in particles with a diameter of around $0.5\ \mu\text{m}$. However, even then the contribution of carbon to the actual open-air light-scattering would be limited to 10%, given that the latter is $25 \times 10^{-4}\ \text{m}^{-1}$. It should finally be considered that two-third of the carbon is from the fireworks.

The open-air light-scattering is five times higher than the dry light-scattering. This difference can only be explained by uptake of water up by the hygroscopic components at the high relative humidities occurring that night. The extra water increases the mass and hence the light-scattering by the particles. Such an increase in light-scattering at higher RH is well-documented (e.g., ten Brink et al., 2000; Bäumer et al., 2008; Fierz-Schmidhauser et al., 2010).

The water accretion can be estimated on the basis of the ionic composition. This can be done even when the actual composition of the salts is not known (e.g., Seinfeld and Pandis, 2006). The reason is that at high humidities, the water accretion of mixed salts and pure components is comparable, because all of these compounds are highly hygroscopic and attract similar amounts of water on an ion-equivalent basis. The uncertainty in this respect is much less than the uncertainty in the value of the relative humidity, which becomes a very sensitive factor in the water uptake close to saturation.

The growth and increase in light-scattering can be calculated when the relative humidity is known. There are measured values for the relative humidity that night and these are 95% and higher. With an uncertainty in hygrometers of 5%, this means that the actual value can be anywhere between 95% and 100%. The associated calculated extra light-scattering by the water has an uncertainty of more than an order of magnitude and the measured RH was thus of no avail here to calculate the growth. It is the other way around. The five-fold larger open-

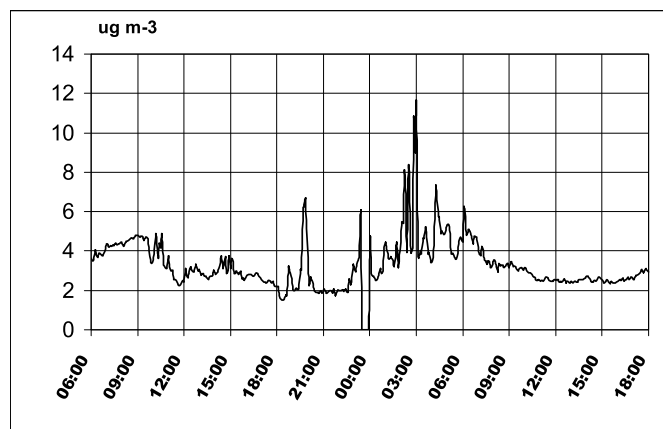


Fig. 3. The concentration of Black Carbon in $\mu\text{g m}^{-3}$ as measured with a MAAP during New Year and New Year's Eve 2009 at the 60 m platform of the CESAR-observatory at Cabauw. Note: there is a malfunctioning of the instrument just before midnight.

air light-scattering compared to the dry light-scattering points to an RH of around 97.5%, as discussed in section 2.1.

The visibility is inversely proportional to the actual open-air light-scattering, as discussed in section 1.1. The visibility at the site was 1200 m at the peak of the advected fireworks aerosol. In the urban source area the visibility must have been much lower. The major source area is almost certainly the city and suburbs of Utrecht at a distance of 9 km to the north-east. This is deduced from the wind direction and a wind velocity of 1 m s^{-1} , see section 2.1.

In Utrecht the mass concentration of fine particulates was determined on an hourly basis at a street station. Based on the ratio between the fine particulate mass at the street station and that at the measuring site the light-scattering and associated visibility was estimated. The extrapolated visibility was as low as 200 m, meaning on the edge of dense fog. Mass concentrations of fine aerosol similar to that in Utrecht occurred at other street locations in the Netherlands, with comparable low visibilities.

High relative humidities are typical for stagnant weather situations in the Netherlands in winter; under such conditions the surface concentrations of the fireworks aerosol are high due to the absence of dispersion. This is confirmed by data on the concentrations of the fine particulate mass concentration and relative humidities during New Year's nights in the respective national networks. It is inferred that the salty components from the fireworks govern the reduction in visibility

Appendix

Hold-up of cations in the sampling columns of the MARGA-sizer and its correction

A complication in the detection of the cations is their presence in the blank. The blank derives from the channel with the absolute filter in the aerosol collection line. This channel follows the measurement of the channel with the impactor with the highest cut-off diameter and thus with the largest amount of material collected. For potassium the average concentration in the blank level and thus carry-over is 9% of the value in the previous channel.

The blank is measured a second time in the measuring cycle. The value for potassium is then close to that observed on days with virtual absence of potassium in the aerosol. The carry-over of potassium is thus limited to one channel. Correction for the carry-over is simple: the value in the blank line is added to that of the previous ($2.0 \mu\text{m}$ impactor) channel. A similar percentage of 9% is added to correct the values in other channels. The correction is actually of little importance there because the measuring cycle starts with the channel with the smallest size-cut and associated lowest concentration. The carry-over to the next channel is thus relatively small.

The hold-up problem is severe for magnesium; there are significant concentrations in the second blank, as seen in Table A1. There the results of the analysis of magnesium in a series of measuring cycles are shown. The data for potassium are given as a reference. Table A1 shows that for magnesium the hold-up c.q. carry-over from the channel with the impactor of $2.0 \mu\text{m}$ to the first blank is 70%, with subsequent carry-over to the second blank channel of again 70% of that value. We assume that the carry-over trails of as in an arithmetic series and that its sum is the full carry-over. This value is added to the channel from which the carry-over originated from, viz. the channel with the impactor with cut-off at $2.0 \mu\text{m}$. On the other hand, there is crossover of analyte from the analysis of the channel with the $1.0 \mu\text{m}$ impactor. Taking this all into account the actual concentration is estimated as about three times that of the measured value.

in general during New Year's nights.

Addendum. We did not yet address the contribution of the light-absorption to the reduction of the visibility. This is exerted by the Black Carbon. Its concentrations, c.f. Fig. 3, as measured with the MAAP, were translated back into the corresponding values of the light absorption coefficient. The peak absorption coefficient thus obtained is $0.6 \times 10^{-4} \text{ m}^{-1}$. This means that the contribution of the absorption is rather negligible compared to that of the open-air light-scattering of $25 \times 10^{-4} \text{ m}^{-1}$.

4. Conclusions

The submicron aerosol from the New Year's fireworks in the middle of the Netherlands in 2009 contained a large fraction of salty products in the form of the ions sulphate, potassium and chloride -in that order- and some magnesium. These are hygroscopic salt mixtures.

The mentioned compounds are for a large part in a size range of particles that most effectively scatter visible light. The aerosol light-scattering in the open air is five times higher than that of dried aerosol. This is explained by the uptake of water by the hygroscopic salts at the high humidities occurring that night. Visibility is the inverse of the light-scattering and the salty products thus, indirectly, governed the visibility.

Aerosol concentrations are high during stagnant weather. In such situations the relative humidity during New Year's night is also high in the Netherlands. The inorganic salty aerosol components are thereby responsible for the low visibilities, be it indirectly, via the uptake of water.

Conflicts of interest

None.

Acknowledgments

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We thank two anonymous reviewers for their valuable suggestions for improvement.

Table A1

Sequence of the concentrations of magnesium and potassium in the aqueous samples of aerosol collected via the collection channels with an impactor of the indicated cut-off diameter (impx.y) or via the lines with an aerosol filter (blank). The samples were taken in the 15 min after the indicated start-time during New Year's night 2009. Aqueous mass concentrations are in the unit ppb. Note: Denuder stands for the gas-denuder that is used to remove gaseous interferences. This line feeds directly into the ion-chromatograph and is also analysed.

Start Time	Mg	K	Collection channel
2:17	12.0	109.9	imp2.0
2:32	0.5	0.7	Denuder
2:47	8.4	15.3	blank1
3:02	6.3	7.5	blank2
3:17	6.1	28.6	imp0.18
3:32	7.5	172.4	imp0.32
3:47	14.1	319.7	imp0.56
4:02	34.6	577.2	imp1.0
4:17	59.4	742.2	imp2.0
4:32	0.0	0.0	Denuder
4:47	34.6	57.3	blank1
5:02	24.6	18.4	blank2

The appreciable hold-up of sample and crossover to the next sample means that the concentration in the channels with smaller cut-offs cannot be assessed with confidence. For that reason the value for magnesium in the 2.0 μm channel was used relative to that of potassium as the reference for the magnesium data in the other channels. The value for magnesium in the 2.0 μm channel was used relative to that of potassium as the reference for the magnesium data in the other channels.

References

- Bäumer, D., Vogel, B., Versick, S., Rinke, R., Möhler, O., Schnaiter, M., 2008. Relationship of visibility, aerosol optical thickness and aerosol size distribution in an ageing air mass over South-West Germany. *Atmos. Environ.* 42, 989–998.
- Dougle, P.G., Veefkind, J.P., ten Brink, H.M., 1998. Crystallization of mixtures of ammonium nitrate, ammonium sulfate, and soot. *J. Aerosol Sci.* 29, 375–386.
- Fierz-Schmidhauser, R., Zieger, P., Wehrle, G., Jefferson, A., Ogren, J.A., Baltensperger, U., Weingartner, E., 2010. Measurement of relative humidity dependent light scattering of aerosols. *Atmos. Meas. Tech.* 3, 39–50.
- Friedlander, S.K., 2000. *Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics*. Oxford University Press, Inc., New York, New York, USA.
- Hidy, G., 1984. *Aerosols: an Industrial and Environmental Science*. Academic Press, London, UK.
- KNMI, 2005. *Handboek Waarnemingen; Ch. 9. Zicht*. versie april 2005. http://projects.knmi.nl/hawa/pdf/Handboek_H09.pdf.
- KNMI, 2009. *KNMI hourly data*. http://www.knmi.nl/klimatologie/uurgegevens_station_348_Cabauw.
- Mensah, A.A., Holzinger, R., Otjes, R., Trimborn, A., Mentel, Th F., ten Brink, H., Henzing, B., Kiendler-Scharr, A., 2012. Aerosol chemical composition at Cabauw, The Netherlands as observed in two intensive periods in May 2008 and March 2009. *Atmos. Chem. Phys.* 12, 4723–4742.
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, second ed. John Wiley and Sons Inc., New York.
- ten Brink, H., Otjes, R., Weijers, E., 2017. Inorganic ions are the main products of the New-Year's fireworks in The Netherlands. Manuscript under review at. *Atmos. Environ.* available from first author of the present manuscript.
- ten Brink, H., Otjes, R., Jongejan, P., Kos, G., 2009. Monitoring of the ratio of nitrate to sulphate in size-segregated submicron aerosol in The Netherlands. *Atmos. Res.* 92, 270–276.
- ten Brink, H., Otjes, R., Jongejan, P., Kos, G., Slanina, J., 2007. An instrument for semi-continuous monitoring of the size-distribution of ammonium nitrate aerosol. *Atmos. Environ.* 41, 2768–2779.
- ten Brink, H., Khlystov, A., Kos, G.P.A., Tuch, T., Roth, C., Kreyling, W., 2000. A high-flow humidograph for testing the water uptake by ambient aerosol. *Atmos. Environ.* 34, 4291–4300.
- ten Brink, H.M., Kruisz, C., Kos, G.P.A., Berner, A., 1997. Composition/size of the light-scattering aerosol in The Netherlands. *Atmos. Environ.* 31, 3955–3962.
- ten Brink, H.M., Veefkind, J.P., Waijers-Ijpelaar, A., van der Hage, J.C.H., 1996. Aerosol light-scattering in The Netherlands. *Atmos. Environ.* 30, 4251–4261.
- Veefkind, J.P., van der Hage, J.C.H., ten Brink, H.M., 1996. Nephelometer derived and directly measured aerosol optical depth of the atmospheric boundary layer. *Atmos. Res.* 41, 217–228.