NATIONAL INSTITUTE OF
PUBLIC HEALTH AND THE ENVIRONMENT
BILTHOVEN, THE NETHERLANDS

Report no. 723301003

Characterization of Episodic Air Pollution
in Cities (CHEAP)

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December 1995

This investigation has been performed on behalf and for the account of the Directorate General Environment (DGM/LE) within the framework of project no. 723301, subproject 723309, "Wintersmog CHEAP"

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ACKNOWLEDGEMENTS

The success of ambient field studies depends largely on the dedication and involvement of all the co-workers. The final report resembles the tip of an iceberg in that most of all the work done remains invisible, underwater. However those responsible for such hidden efforts should not remain invisible. Therefore the authors wish to express their gratitude to Mr. H. Bos, Mr. J. van Hellemont, Mrs. E.M. van Putten, Mr. T. Regts, Mr. J.W. Uiterwijk, Mr. J. Venema and Mr. H. Wiese for their expert assistance during the CHEAP study. The authors also want to thank the co-workers of the Laboratories for Inorganic Chemistry (LAC) and Organic-analytical Chemistry (LOC) for the various analyses of air pollutants.
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ABSTRACT
Adverse health effects have been associated with increased levels of air pollution. To better understand the behaviour and sources of a number of air pollutants, in particular fine suspended particulate matter, a descriptive study was undertaken in the Netherlands in the City of Amsterdam and in a rural area near Biddinghuizen, 50 km north-east of Amsterdam. Increased levels of particulate matter were due to the following different conditions:
- New Year’s Eve, with very high but short-lived concentrations,
- high wind speeds, causing resuspension of settled dust, and
- stagnant weather conditions, with low rates of pollutant transport.
During winter-smog episodes the contribution (on a mass basis) of PM1 (submicron particles below 1 μm) to PM10 was found to increase from circa 10 to 20%.
The contribution of secondary aerosol definitively increased during such stagnant episodes (over 70%), clearly dominating the observed PM10 levels; the contribution of soot increased only marginally.
The good correlation observed between PM1 levels and the compounds emitted by mobile sources (like benzene, CO and aldehydes) suggests that traffic is the main source for PM1. The Principal Components Analysis applied also confirms the dominating contribution of traffic-related particulate matter to PM1.
Traffic-related particulate matter (=PM1) only slightly contributes to the mass of PM10. Consequently, a decrease in traffic-related particulate matter only results in a slight (definitively non-proportional) decrease of PM10 mass. Vice versa, a decrease of PM10 does not necessarily imply a proportional decrease in traffic-related particulate matter. Hence, the slight difference between PM10 levels observed in urban and rural areas suggests that due care should be exercised in associating health effects with PM10.
The observed regression of PM1 on benzene might prove useful to estimating levels of PM1. The advantage of selecting a commonly measured compound such as benzene for this purpose offers the possibility to assess exposure retrospectively.
SAMENVATTING
Het gedrag van Fijn Stof (PM10) is onderzocht in een veldstudie op een tweetaal karakteristieke locaties, nl. stadsachtergrond (Amsterdam) en een landelijke omgeving (Biddinghuizen). Tijdens wintersmog verdubbelt de bijdrage van PM1 (submicron deeltjes met afmetingen kleiner dan 1 μm) aan PM10 van circa 10 tot 20%. Het secondaire aerosol vormt de dominante factor (bijdrage aan PM10 meer dan 70%); de bijdrage van roet blijft beperkt. De goede correlatie tussen PM1 en verkeersgebonden componenten als benzeen, CO en aldehyden suggereert verkeer als de voornaamste bron voor PM1. Het verkeersgebonden PM1 draagt marginaal bij aan PM10. Dwz. een afname in verkeersgebonden PM1 leidt slechts tot een marginale afname van PM10. Omgekeerd houdt een afname in PM10 niet een evenredige afname van PM1 in.
1. INTRODUCTION

Recent epidemiological studies have raised awareness in the regulatory and the scientific field that adverse health effects could be associated with air pollution in cities during winter-type smog episodes, even when the air quality indicator is well below the alert level. Furthermore, these health effects could be associated with levels of fine suspended particulate matter (PM10) frequently occurring in the Netherlands. These observations have lead to the recognition that the indicator based on levels of sulphur dioxide (SO₂) and PM10 is not adequate for indicating air quality (Annema et al., 1995; van Aalst et al., 1995). The parameter PM10 must be considered as a 'container' as it does not describe the physico-chemical nature of the particulates; particle-size distribution and adsorbed chemical substances are ignored.

Current insights are based on epidemiological and toxicological data collected at times when air pollution was dominated by SO₂ and TSP (total suspended particulate matter). Since then, SO₂ levels have dropped due to improved combustion and abatement technologies, while levels of particulates have not. Furthermore, it is widely acknowledged that the composition of air pollution has changed considerably over time: various sources have become less important, whereas the contributions of others have increased. The nature of episodic air pollution is unclear due to uncertainties about its sources and the fate of air pollutants released in the urban area or transported from outside. Observations in the Dutch National Air Quality Monitoring Network NAQMN (Aben et al., 1993) indicate that PM10 levels in rural and urban areas do not differ significantly; levels in cities are at the most 10-20% higher than in rural areas. All these findings imply that epidemiological observations made at different sites and different times, but with comparable levels of particulate matter, cannot be explicitly compared. Compounds causing adverse health effects caused by one set of particles might differ substantially from another, both in level and in nature.

This report describes the results of a descriptive study undertaken in the City of Amsterdam and in a rural area near Biddinghuizen, The Netherlands, to better understand the behaviour and sources of a number of air pollutants. The measurement results of a short winter campaign, focusing on the contribution of traffic emissions to particulate matter levels, are evaluated. Section 2 elucidates the study design and the monitoring schemes employed. Sections 3 and 4 give an overview and evaluation of the monitoring results for selected periods of high PM10 levels as opposed to low levels.
2. METHODS and MATERIALS

2.1. Study design

2.1.1. Spatial resolution
In recent years, winter-smog episodes have occurred in the Netherlands during east-west circulations and under stagnant weather conditions. The selection of the monitoring locations was based on this observation.

Amsterdam was selected as the urban monitoring site since the impact of industrial emissions was considered here to be less than in all other major cities in the Netherlands, and because the area east of Amsterdam is mainly rural. In the city, a monitoring site was selected within the perimeter of the 'Revalidatie Centrum' (Rehabilitation Centre) Amsterdam (RCA) on the Overtoom, a main traffic street in Amsterdam-West. This location, with a relatively unobstructed transport of air from the east, could be considered for registering city background emissions. Airflow from the nearby heavy-traffic street (Overtoom) was obstructed by a narrow canyon-like road, only incidentally used for delivery to the RCA. Details of the urban site are given in Figure 1.

The rural monitoring site was located in the Flevoland polder 50 km north-east of the urban site. The monitoring equipment was placed at the NAQMN station, Biddinghuizen, situated within the perimeter of a small research farm. In all directions the surroundings on all directions consisted of arable land. Occasionally, farmer transport vehicles passed within a short distance of the monitoring station. Details of the rural site are given in Figure 2.

2.1.2. Temporal resolution
Monitoring air pollution levels in cities requires a temporal resolution that corresponds with the variation in time of emissions of likely important sources. Traffic was assumed to be the predominant source in cities, adding air pollutants to an air mass flowing over the city after passing over rural areas. This air mass may have been pre-loaded with pollutants emitted by remote sources abroad or formed by atmospheric reactions of constituents during long-range transport. Air pollutant levels in cities themselves are often parallel to traffic intensity combined with the effect of the mixing-layer height.

For continuous measurements a time resolution of one hour was considered sufficient to observe the dynamics of these pollutant levels. For measurements requiring
longer integration times, the sampling periods were selected such that traffic intensity peaks were included as completely as possible in a single sample. The selection of the sampling periods was based on findings in other studies (Bloemen et al., 1993), revealing that morning concentration peaks started as early as 06:00 h and lasted until 10:00 h. Peaks in the afternoon were not so distinct as peaks in the morning and levels were usually low again at 19:00 h. These non-continuous measurements were performed at regular intervals based on cycles of 3 or 6 days.

2.1.3. Parameter selection

The various monitoring parameters, with the reason for selection, are given in Table 1.

Table 1: Groups of monitoring parameters

<table>
<thead>
<tr>
<th>Group</th>
<th>Rationale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic gases</td>
<td>CO₂, NO₂ and SO₂ are indicators for emissions from mobile sources and other combustion processes. SO₂ is presently used as one of the terms of the indicator for winter-type smog. HNO₃, HNO₂ and NH₃ are precursors of secondary aerosol.</td>
</tr>
<tr>
<td>Secondary aerosol</td>
<td>Ammonium sulphate and ammonium nitrate are the main constituents of secondary aerosol and indicate the contribution of long-range transport.</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly Aromatic Hydrocarbons, measured as a sum, serve as an indicator for the emissions of combustion processes, in particular traffic emissions. Patterns of individual PAHs might be used to confirm the nature of the source.</td>
</tr>
<tr>
<td>(V)VOC</td>
<td>(Very) Volatile Organic Compounds are emitted by mobile sources during operation as well as at rest through evaporation and various urban and industrial activities. The large number of volatile compounds enables source apportionment by multivariate data processing.</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Aldehydes are emitted by combustion processes as well as being formed in the atmosphere. The latter source might be less relevant during wintertime.</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>Several sources of heavy metals are active in an urban area. The large number of elements observed allows multivariate data analysis for source apportionment.</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>Particulate matter (PM10) is considered the key parameter to explaining adverse health effects associated with air pollution during winter-type smog. For this purpose, the particle-size classification is thought to be essential to describe human exposure. Soot serves as a measure of the carbonaceous part of the ambient aerosol.</td>
</tr>
<tr>
<td>Meteorology</td>
<td>Temperature, relative humidity and the mixing-layer height are relevant parameters to explaining variations in the other parameters.</td>
</tr>
</tbody>
</table>

The selection of the parameters was based on the perceived information these parameters could render for the following objectives: (i) phenomenological description of air pollution in cities to provide information on composition and particle-size distribution, (ii) source recognition and apportionment.
2.2. Monitoring methods

2.2.1. Monitoring scheme

Only the parameters that could be measured with operational methods were selected for the groups in Table 1. These parameters were monitored using different temporal schemes (see Table 2).

Table 2: Monitoring parameters

<table>
<thead>
<tr>
<th>Group</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters monitored continuously with an integration time of one hour.</td>
<td>CO, NOx, SO2</td>
</tr>
<tr>
<td>Inorganic gases</td>
<td></td>
</tr>
<tr>
<td>PAH</td>
<td>PAH total</td>
</tr>
<tr>
<td>VVOC</td>
<td>C2-C8 aliphatics, C2-C8 olefins, C0-C4 aromatics</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>PM10</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>soot (urban site only)</td>
</tr>
<tr>
<td>Meteorological</td>
<td>temperature, relative humidity, mixing-layer height (Bilthoven)</td>
</tr>
</tbody>
</table>

Samples collected over periods of 11 hours (night-time starting at 19:00 h) or 13 hours (daytime starting at 06:00 h) every 3rd day during the campaign period.

Heavy metals               | all those measurable with ICP-MS (see Appendix A7)               |

Samples collected over 11 hours (night-time) or 13 hours (daytime) spread over four days per cycle of six days during non-episodic situations. During episodic situations the sampling frequency was increased to collect samples over every six hours starting at 19:00 h.

VOC                       | C6-C16 aliphatics, benzene and C6 alkyl aromatics, isoprene, terpenes |
VOX                       | C6-C10 chlorinated aliphatics, C0-C4 chlorinated aromatics       |
Aldehydes                  | formaldehyde, acetaldehyde, acroleine, crotonaldehyde, benzaldehyde |

Samples collected over periods of 11 hours (night-time) or 13 hours (daytime) every 6th day during non-episodic situations and every 3rd day during episodes.

Inorganic gases            | NH₃, HNO₂, HNO₃                                                    |
Secondary aerosol          | NO₃⁻, SO₄²⁻, NH₄⁺, Cl⁻, H⁺                                       |

Samples collected for 24 hours starting at 19:00 h every 6th day during non-episodic situations and every 3rd day during episodes.

PAH                       | PAHs (16 EPA)                                                    |

Parameter monitored every 6th day, and partly continuously during episodic situations, with an integration time of one hour.

Particulate matter         | size distribution 0.01 - 0.8 µm and 0.5 - 20 µm (urban site only) |
Monitoring started on 7 December 1993 at 00:00 h and was continued until midnight 6 March 1994. The period was divided in 15 cycles of 6 days. For reasons of convenience a derived time unit was used: cheaphour - defined as the time in hours past 7 December at 00:00 h.

2.2.2. Monitoring stations
The monitoring equipment was installed in a semi-mobile station, the VOCCARe, developed by the Air Research Laboratory. This station is a 8-m long trailer, equipped with zero air generators and gas cylinders for calibration of the various monitors. Sampling of various compounds and synchronized operation of all monitors was controlled by a dedicated processor. Data was acquired using various microprocessors and transferred at regular intervals to the laboratory using a modem connection. The station is described in detail elsewhere (Bloemen et al., 1995a).

2.2.3. Analytical methods
In this section a brief description of each method is given.

CO was measured with Thermo Electron Instruments monitors model 48W, based on the gas filter correlation method, NOx with Ecophysics model CLD 700 AL chemiluminescence analyzers, and SO2 with Thermo Environmental Instruments model 43W monitors, based on UV pulsed fluorescence. The CO and SO2 monitors are also used in the NAQMN. The NOx monitors use the same measuring principle as those applied in the NAQMN; however, the manufacturer is different. The monitors were calibrated daily using zero air and certified calibration mixtures every six days (CO and SO2) or every day (NO) around midnight.

Particulate matter was measured in various ways. At the urban site, PM10 was measured using a FAG FH 62-I-N β dust monitor (as in the NAQMN), based on absorption of β-electrons through a particle laden filter. At the rural site a TEOM model 1400a from Rupprecht & Patashnick, based on the change of the mechanical eigenfrequency of a particle-laden filter. The β-dust monitor was calibrated using specially manufacturer supplied calibration foils. The TEOM monitor was calibrated using certified particle-laden standard filters.

The size distribution of the ultra-fine particle fraction (0.01-0.8 μm) was measured using a Scanning Mobility Particle Sizer, made up of an electrostatic classifier model TSI-3071 and a condensation nucleus counter model TSI-3020. The size selectiveness of the
instrument results from the size-dependent mobility of charged particles in an electrical field.

The size distribution in the range 0.5 - 20 μm was measured using a TSI Aerodynamic Particle Sizer model APS-3020. The size selectiveness of the instrument results from the particle-size dependent velocity lag of particles exiting a thin-walled orifice. The size determination was calibrated with a set of monodisperse particles, resulting in a small correction factor for the size determination. No mass calibration was carried out.

Secondary aerosol (sulphate, nitrate, ammonium, chloride and H⁺) and the inorganic gases HNO₂, HNO₃, NH₃ were measured using an annular denuder system (ADS) supplied by University Research Glassware (Carrboro, USA). Air was sampled at a flow rate of 1 m³ h⁻¹ through three successive annular denuders coated with Na₂CO₃ (first and second) to collect acidic gases and with citric acid (third) to collect NH₃. A filter pack consisting of a Teflon filter was used for collection of particles and a nylon filter for collection of HNO₃ eventually released from the Teflon filter by dissociation of volatile ammonium nitrate. After sampling, denuders and filters were extracted with de-ionized water and analyzed for the relevant components using Ion Chromatography for the anions, an Indophenol colorimetric method for ammonium and coulometric titration for H⁺. The ADS method is described in detail in Mennen et al. (1992).

Heavy metals were determined on so-called medium-volume filter samples (MVS). MVS systems with a flow rate of some 10 m³ per day were used. The dust-laden filters were hydrolyzed and analyzed using inductive-coupled plasma mass spectrometry (ICP-MS). Initially, all elements emerging as peaks in the mass spectrogram were used. Calibration carried out for a selection of elements was only semi-quantitative.

PAH was monitored using Kimessa instruments model LQ1E ARP, based on the photoelectric emission from the PAH adsorbed on submicron particles. Soot (as a measure of the carbonaceous part of the ambient aerosol) was measured using a GIV aethalometer model AE-10-M, based on absorption of white light through a particle-laden filter. The instrumental output (in mV) was not converted in equivalent μg m⁻³ soot (due to lack of an appropriate calibration curve). Both these monitors were calibrated by the respective manufacturers and data obtained were used without further processing other than averaging over one hour.

VOC were collected during 40 minutes every hour and subsequently injected on a chromatographic column for separation followed by flame ionization detection. Quantification and identification were done on the basis of the calibration function and
reference retention times obtained for each compound by analyzing calibration gas mixtures in nitrogen (Bloemen and Burn, 1993; Bloemen, 1993).

VOC and VOX (halogenated volatile organic compounds) were collected on activated charcoal tubes and eluted in the laboratory with CS₂. The eluent was analyzed gaschromatographically using simultaneous flame ionization and electron capture detection. Quantification and identification was performed using calibration functions and reference retention times obtained for each compound by analyzing calibration mixtures in CS₂ (Bloemen and Burn, 1993; Bloemen, 1993).

Aldehydes were collected on DNPH-coated cartridges at a flow rate of 300 ml min⁻¹ on which they were instantly converted to stable hydrazone derivatives. In the laboratory the derivatives were eluted with acetonitril and analyzed with reversed-phase high-pressure liquid chromatography. Calibration was carried out with standard solutions of the aldehydes added to DNPH-coated cartridges.
3. RESULTS

The presentation of the data is guided by the hypothesis that during winter-type smog conditions the levels of especially particulate matter are increased when compared to normal winter conditions. Subsequently the following relevant periods can be defined (see Figure 3 and Table 3). The periods are coded chronologically.

*Period A*

During this period, high levels could be traced back to air pollution caused by fireworks emitted around New Year’s Eve. This period was considered non-relevant, although levels were extremely high, particularly during the first hour of 1994. Air pollution caused by fireworks on New Year’s Day is discussed extensively by Noordijk 1994).

*Period B*

In the morning of January 11, PM10 levels increased to approximately 70 µg m⁻³.

*Period E*

This period (February 21 - 26) lasted longer than the two previous ones, and can be considered a pseudo-episode - a period with increased, but not as high, levels as defined for a real episode.

*Period C and D*

Period C (between noon February 11 and 13) was selected because the contribution of fine particles was high. Period D (noon February 13 to 15) was selected because high PM10 concentrations were observed at the rural NAQMN stations in the east and north of the country, and at Biddinghuizen. The first period was followed immediately by the second. The transition occurred at noon on February 13, 1994. In the morning of that day wind speed increased to well over 10 m s⁻¹ at noon and remained high until noon February 15, 1994 (Figure 4).

*Periods 0a and 0b*

The two periods 0a (January 16 - 17) and 0b (January 29), with low concentrations of particulate matter, were selected as a contrast to the aforementioned high-level periods. Although other periods with low-particle concentrations were available, only these two periods were selected because the particle-size distribution was measured then.
Table 3: Characterization of periods with low and high particulate-matter levels

<table>
<thead>
<tr>
<th>Period</th>
<th>Date</th>
<th>cheaphour</th>
<th>Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>0a</td>
<td>16-01-1994 20:00</td>
<td>980 - 1008</td>
<td>low levels of particulate matter</td>
</tr>
<tr>
<td></td>
<td>17-01-1994 24:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0b</td>
<td>29-01-1994 00:00</td>
<td>1272 - 1296</td>
<td>low levels of particulate matter</td>
</tr>
<tr>
<td></td>
<td>29-01-1994 24:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>31-12-1993 00:00</td>
<td>576 - 624</td>
<td>extreme high concentrations of particulate matter concurrent with fireworks emissions</td>
</tr>
<tr>
<td></td>
<td>01-01-1994 24:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>11-01-1994 00:00</td>
<td>840 - 876</td>
<td>high levels of particulate matter</td>
</tr>
<tr>
<td></td>
<td>12-01-1994 12:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>11-02-1994 00:00</td>
<td>1584 - 1644</td>
<td>low levels of particulate matter</td>
</tr>
<tr>
<td></td>
<td>13-02-1994 12:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>13-02-1994 12:00</td>
<td>1644 - 1692</td>
<td>high levels of particulate matter concurrent with strong winds</td>
</tr>
<tr>
<td></td>
<td>15-02-1994 12:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>21-02-1994 00:00</td>
<td>1824 - 1944</td>
<td>high levels of particulate matter remaining high for some days (pseudo-episode)</td>
</tr>
<tr>
<td></td>
<td>26-02-1994 00:00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Period average values and extremes (min - max) are given in Appendix A; the latter values are only given if data are available for a considerable fraction of the period. The often large range is due to the diurnal pattern.

The behaviour of a number of components during the selected periods is briefly presented in the following.

*Sulphur dioxide*

The averaged levels of SO₂ at the urban site show a base level of 4 to 6 ppb. During the periods B, D and E, levels are increased by a factor of 1.2 to 2. At the rural site a base level of approximately 2 ppb is shown. During periods D and E the average levels are to 2 to 5 times the base level. The increase during period D at the rural site is striking as the dispersion due to the strong winds is high. The higher levels during periods D and E might be due to long-range transport from Eastern Europe.

*Carbon monoxide and nitrogen oxides*

The levels of the parameters indicative for combustion processes CO and NOₓ are high during the control period 0a. In fact, these levels are nearly the highest measured
throughout the selected periods. These levels concur with the high levels of benzene and BETX (see further on in this document), suggesting an emission impact of (nearby) mobile sources. However, the levels of CO and NO\textsubscript{x} at the rural site are slightly increased as well when compared to the levels of periods A, C and D; these increases are in agreement with observed increased levels of benzene and BTEX. Again, the periods B and E show CO and NO\textsubscript{x} levels higher by a factor of 2 than for periods 0b, A, C and D at the urban site. At the rural location, the levels of both CO and NO\textsubscript{x} increased by a factor of 2 to 3.

*Particulate matter*

The levels of PM\textsubscript{10} measured at the rural and urban sites differ only slightly. This holds for the average as well as the extreme values. Previous observations in NAQMN support this. Elevated average concentrations are only measured during period D (strong winds) and the 'pseudo-episode' E. The average concentrations during periods D and E are between 45 and 65 µg m\textsuperscript{-3}, i.e. approximately 2 to 3 times the levels of the control periods 0a and 0b; the maximum values range from 100 - 250 µg m\textsuperscript{-3}.

*Secondary aerosol*

Secondary aerosol, made up by the total concentration of ammonium nitrate, ammonium sulphate and ammonium chloride, is low (4.2 µg m\textsuperscript{-3}) at the urban site, and slightly higher (7.6 µg m\textsuperscript{-3}) at the rural site during the control period 0a. During the period 0b low secondary aerosol levels (1.6 µg m\textsuperscript{-3}) are measured. During these periods the secondary aerosol concentration accounts for 20 and 40% of the measured PM\textsubscript{10} fraction for the urban and the rural sites, respectively.

The periods B, C and E, are characterized by equal levels concurring at both the urban and rural sites. These levels are 10 (period B and C) to 30 times (period E) higher than the concentrations measured during the control period 0b and account for 65 - 80%, and well over 70%, of the measured PM\textsubscript{10} levels for the urban and rural sites, respectively.

*PAH and soot*

The status of the control period 0a is challenged by the levels measured with the PAH monitor and the aethalometer. The levels are again among the highest measured during the project period. The PAH levels during the periods A, B and E are 50 - 70% higher than during the periods 0b, C and D. This is only partly supported by the aethalometer.

Data for total PAH, as the sum of all the individually measured PAHs, are only available
for the periods D and E. The ratio of the concentrations of total PAH measured during
these periods is about 2. For the individual PAHs occurring at relatively high levels, the
ratios are considerably different, indicating different patterns.

PAH measured with the PAH monitor cannot explicitly be compared with the total PAH,
calculated as the sum of all the individually measured PAHs. The sensitivity of the various
PAH will be different, hence different mixtures of PAH at the same mass concentration
will result in a different signal from the PAH monitor.

Heavy metals
Many of the elements adsorbed on particulate matter are detected by ICP-MS at
concentrations just above the determination limit. The semi-quantitative results issuing from
this method are emphasized; hence, outcomes for individual elements can be intercompared
but absolute concentrations might deviate by a factor of 3.

Ni and to a lesser extent Cu seem to be related to fireworks emission. When compared to
the control periods, Pb, Zn and V show higher concentrations at both sites during all the
periods (no data are available for period C). Cu is only higher during periods A and B,
while Mn shows higher levels during periods B, D and E.

Volatile organic compounds (VOC)
Many volatile organic compounds have been measured, many of which have originated
from similar sources. Data on a selection of compounds are presented in Appendix A.
The levels of benzene at the rural site support its city background nature. During non-
(pseudo-)episodes (periods 0a, C and D) the concentrations vary between 1.7 and 2.9 µg
m⁻³ and are slightly higher than at the rural station (1.2 - 1.9 µg m⁻³). Again, the average
concentration during the control period 0a is high (5.2 µg m⁻³). High concentrations are
also found during the pseudo-episodes B and E (3.2 and 4.5 µg m⁻³).

The contribution of benzene to the composition of light aromatics (BTEX - benzene,
toluene, ethylbenzene and xylenes) is rather constant during the first period of the project
(period A - 0a), ranging from 15 to 18%. During the second part of the project period (C-
E) the contribution is slightly higher (22-28%). This suggests that the aromatics originate
from the same source or set of sources, with a constant emission pattern, most probably
traffic. The slight increase in the contribution of benzene might be caused by a different
fuel formula, starting in February 1994.

Three of the chlorinated hydrocarbons mentioned in Appendix A show substantial spatial
variation. Trichloroethene, tetrachloroethene and 1,1,1-trichloethane, used, among other applications, for cleaning, are found in higher concentrations in the city than in the rural area. This variation is not strong for tetrachloromethane. The difference between the urban and rural location vanishes at high winds (period D).

The more volatile organic compounds (ethane, acetylene, n-propane, n-propene, n-butane and 1,3-butadiene) show various degrees of spatial and temporal variation. Acetylene is not measured above the detection limit of the analytical method (0.05 μg m⁻³) at the rural site except during the period with high wind speeds and the pseudo-episode E. The concentration (again excluding period A) varies between 3.7 and 4.4 μg m⁻³; only during period E are the levels substantially higher (7.2 μg m⁻³, i.e. circa 25 times the rural background).

**Aldehydes**

Only the two aldehydes, formaldehyde and acetaldehyde, show detectable concentrations during the various periods. Formaldehyde is relatively high in both locations during periods 0a and B, when the concentrations at the urban site are about twice those at the rural site. During the pseudo-episode E the concentrations at the urban site are moderate, with an urban/rural ratio of approximately 4.2. The diluting effect of the high wind speed is observed during periods C and D. Acetaldehyde is also detected at high concentrations during periods 0a and B at the urban site, while the rural concentrations remain low. The concentrations of period E are again moderate with an urban/rural ratio of 3.9. In contrast to many other pollutants, the pseudo-episode is marked by lower aldehyde concentrations than period B. The control period 0a shows again the highest levels.
4. DISCUSSION

4.1. Validation

In this section attention is focused on the validation of measured data, particularly:
- assessment of possible sample losses during collection of the particulate matter.
- a comparison of measured PM10 data against results of the NAQMN.
- a comparison of full size distributions and measured PM10 data.
- a comparison of benzene results from the VOC and VVOC measurement methods.

4.1.1. Sample collection losses

Air was sampled via several inlets and sampling tubes, depending on the position and measuring principle of the various instruments. For the methods used to measure particulate matter, this implies that particles may be 'lost' during transport from the ambient air to the instrument due to a non-perfect aspiration efficiency at the inlet of the tube, sedimentation inside the tube (if the tube is not mounted vertically) or impaction at the inlet or inside the tube (if the tube is bent). These losses depend on the wind velocity, the flow inside the tube, the dimensions, the shape of the tube and inlet, and the size and shape of the particles. Due to the above losses, the measured concentration is an underestimation of the real one.

These losses were estimated for each particle-measuring instrument (i.e. the APS, SMPS, ADS, MVS, PAH monitor and aethalometer), using various semi-empirical equations given by Laktionov (1973), Durham and Lundgren (1980), Vincent (1989), Hangal and Willeke (1990a; 1990b) and an empirical fit of the data from Cheng and Wang (1981). Losses were estimated for temperatures ranging from -15°C to 5 °C, wind velocities from 1 to 8 ms⁻¹ and particle diameters between 0.1 and 100 μm. In the equations applied, the particles are assumed spherical. Losses caused by static charges, which might be built up on the sampling tubes, were not accounted for.

For the FAG and TEOM monitor these losses were not estimated because these instruments are already supplied with a PM10 inlet. No losses are expected in the sampling tube between the inlet and the instrument.

The results of the estimations showed that, except for the MVS and APS, the particle losses in the size range of each instrument were less than 5 to 10% for all relevant weather conditions. For example, the loss of 0.8 μm particles in the inlet configuration of the SMPS is only 7% at 8 ms⁻¹ and 5 °C, and even less at other conditions and lower
particle size. The loss of 1-μm particles in the inlet configuration of the aethalometer is 10% at 8 m s⁻¹ and 5 °C, and less at other conditions and smaller particle size. Since most soot particles are smaller than 1 μm, the error in the concentration measured by the aethalometer will be small.

For the MVS and APS, the particle losses (shown in Table 4) have not been corrected for in the further analysis of the data measured with these instruments. Indeed, the bulk of the particles larger than 10 μm were only encountered during the high wind period D.

Table 4: Particle losses (%) for MVS and APS

<table>
<thead>
<tr>
<th></th>
<th>Particle size</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wind</td>
<td>&lt; 0.2 μm</td>
<td>5 μm</td>
<td>10 μm</td>
</tr>
<tr>
<td>MVS</td>
<td>1 m s⁻¹</td>
<td>negligible</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>8 m s⁻¹</td>
<td>10</td>
<td>60</td>
<td>99</td>
</tr>
<tr>
<td>APS</td>
<td>1 m s⁻¹</td>
<td>negligible</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>8 m s⁻¹</td>
<td>10</td>
<td>40</td>
<td>88</td>
</tr>
</tbody>
</table>

4.1.2. Comparison of measured PM10 data vs. NAQMN

The urban station in Amsterdam (RCA) had not been used before and hence no information on the impact of any unknown nearby sources existed. The rural station at Biddinghuizen was located at the site of the NAQMN and extended data sets collected over the years confirm the classification as rural background. The temporal resolution was such though that short-term active nearby sources could produce misleading indications. Furthermore, the TEOM PM10 monitor implemented at the rural Biddinghuizen site had not yet been subjected to a genuine field test. Therefore results obtained at the monitoring sites were compared with data collected at nearby or comparable stations of the NAQMN or at stations operated by the Municipality of Amsterdam, using the same type of FAG FH 62-I-N PM10 instruments (Omeqam, 1994). This validation step became more important since the air pollution levels did not reach the limits set for winter-type smog episodes. The artefacts caused by malfunction of the instrumentation or the impact of nearby sources then become more relevant.
The PM10 measurements at the Amsterdam site were compared to those made at the NAQMN station, Amsterdam-Noord (NAQMN-520). After correction for three outliers the variance coefficient (R square) was 69% and the regression was:

\[ \text{Amsterdam site} = 4.8 + 1.06 \times \text{NAQMN-520} \ (g \ m^{-3}) \]

Considering the distance between the stations this indicates good agreement for the 1652 measurement results obtained during the campaign period. The daily averaged values at the Amsterdam site also showed good agreement with the Omegam results obtained at the Sarphatistraat (Amsterdam-Oost) and the IJsbaanpad (Amsterdam-Noord) at moderate levels. However, at the high end of the range, levels at the Amsterdam site remained substantially lower. This emphasizes the city background nature of the Amsterdam CHEAP site.

For the Biddinghuizen site the levels were compared to those at the rural background NAQMN-928 station (Witteveen), 75 km to the north-east of Biddinghuizen and 130 km north-east of Amsterdam. The variance coefficient (R-square) was 37% and the regression was

\[ \text{Biddinghuizen site} = 2.2 + 0.86 \times \text{NAQMN-928} \ (g \ m^{-3}) \]

The poor correlation might be due to the use of different PM10 monitors at the LML (FAG) and rural (TEOM) sites. The two monitors were compared during a short measuring campaign on the premises of the Institute. The variance coefficient (R-square) was 74% and the regression given by:

\[ \text{TEOM} = -0.8 + 0.64 \times \text{FAG} \ (g \ m^{-3}) \]

This indicates a systematic difference between the monitors for yet unresolved reasons. Taking this into account, the following corrected 'FAG-compatible' PM10 values at the rural site are implied:

\[ \text{Biddinghuizen site} = 1.34 \times \text{NAQMN-928} \]

Once again, considering the distance between the stations this indicates a fair agreement of the Biddinghuizen site with the other rural background station. Considering the above observations, the authors feel comfortable about their PM10 results.

4.1.3 Comparison of PM10 measured vs. PM10 calculated from APS data

The Amsterdam particulate matter concentrations measured with the PM10 monitor were compared with calculated ones, starting from the observed SMPS/APS particle-size distributions and the standardized PM10 cut-off curve (ISO7708, 1995). Appendix B gives the details of this procedure.
The variance coefficient (R-square), based on 845 hourly averaged values, was just 34% and the regression given by

\[ PM_{10\,calc} = 1.18 \times PM_{10\,mea} + 5.8 \, (g \, m^{-3}) \]

Taking into account the observed systematic undersampling of the PM10 sampling head used of circa 25% (Holländer et al., 1990; CEN, 1995), the following corrected relationship is implied:

\[ PM_{10\,calc} = 0.9 \times PM_{10\,mea} \]

Note that the correlation coefficient could be influenced by various factors, including density (assumed to be 1 in the calculation), shape (assumed to be spherical), variation of the inlet sampling efficiency of the APS with wind velocity and losses in the APS sampling tube.

Another important factor is the hygroscopic particle-growth factor. This factor depends on the relative humidity and the hygroscopic nature of the particles. Adsorption of moisture at relative humidities above 70% results in larger particles measured by the APS, whereas the air stream containing the particles collected by the PM10 monitor is dried, thus reducing the particles' size. In qualitative accordance with this reasoning, the ratio \( PM_{10\,calc} / PM_{10\,mea} \) increases with increasing relative humidities (see Table 5 and Appendices A1 & A3).

### Table 5: Relative humidity and particle growth

<table>
<thead>
<tr>
<th>Period</th>
<th>Relative humidity (%)</th>
<th>Average ratio ( PM_{10,calc} / PM_{10,mea} ) Uncorrected *</th>
<th>Average ratio ( PM_{10,calc} / PM_{10,mea} ) Corrected *</th>
</tr>
</thead>
<tbody>
<tr>
<td>0a</td>
<td>84.5 ± 8.2</td>
<td>\approx 1.0</td>
<td>\approx 0.75</td>
</tr>
<tr>
<td>0b</td>
<td>80.4 ± 11.4</td>
<td>\approx 0.75</td>
<td>\approx 0.55</td>
</tr>
<tr>
<td>A</td>
<td>85.7 ± 5.0</td>
<td>\approx 1.65</td>
<td>\approx 1.25</td>
</tr>
<tr>
<td>B</td>
<td>90.6 ± 3.3</td>
<td>\approx 4.4</td>
<td>\approx 3.3</td>
</tr>
<tr>
<td>C</td>
<td>82.4 ± 6.8</td>
<td>\approx 1.7</td>
<td>\approx 1.3</td>
</tr>
<tr>
<td>D</td>
<td>55.8 ± 8.8</td>
<td>\approx 0.95</td>
<td>\approx 0.7</td>
</tr>
<tr>
<td>E</td>
<td>84.9 ± 7.8</td>
<td>\approx 2.85</td>
<td>\approx 2.15</td>
</tr>
</tbody>
</table>

* (Un)corrected for the aforementioned undersampling of 25%

The overall regression factor of approximately 0.9 shows that the data of both the APS and the PM10 monitors are reliable. The effect of PM10 undersampling has not been taken into
account in the further analysis. PM1 and PM2.5 concentrations were also calculated. Clearly, the absolute values have to be considered with due care, but the relative contributions of calculated PM1 and PM2.5 to calculated PM10 can be genuinely applied.

4.1.4. Comparison of benzene results from VOC and VVOC measurements
Benzene was measured with two analytical techniques (VOC and VVOC). In general, the results are in good agreement, except for the measurements at the urban site during periods C and E. This might partially be caused by different time coverage of the period by the followed sampling scheme. It is known though that occasionally a coeluting compound present in the sample obstructs proper determination of benzene when using the VOC method (Bloemen et al., 1990). Furthermore, the ratio of the concentrations on toluene and benzene is usually within the range of 1.8 - 3.0 (LML, 1993). The results of the VVOC method comply with this and hence the VVOC results will be used for the evaluation of aromatic hydrocarbons.

4.2. Period characterization
In this section the discussion focuses on:
- phenomenology of PM10 in terms of the contribution of PM1 and PM2.5.
- indicator components for winter-type episodes, in this case, traffic.
- source apportionment as a means to possibly identifying various sources.

4.2.1. PM10 phenomenology
Periods 0a and 0b: Control periods
The control periods, of which 0a started on Sunday evening and lasted till Monday night and of which 0b a complete Saturday, show similar PM10 concentrations. Both were measured and calculated (average 20 μg m⁻³, maximum 35 μg m⁻³). Since the control periods were taken during the weekend, possible rush hour effects do not play an important role. The particle-size distribution during period 0a (Figure 5) shows a large contribution of large particles being constant throughout this period.

Period A: Fireworks
Extremely high levels of particulate matter are measured during this period: 933 and 117 μg m⁻³ at the urban and rural sites, respectively. These high peaks do not result in high period average values due to the low concentrations during the remaining time.
The size distribution shows a substantial mass fraction of large particles between 15 and 40 µm during the peak hours of the fireworks. During the fireworks the contribution of PM$_{1_{\text{calc}}}$ to PM$_{10_{\text{calc}}}$ remains approximately constant, whereas the contribution of PM$_{2.5_{\text{calc}}}$ shows a steep decrease. This implies that the particulate matter consists of very fine as well as extremely large particles.

*Period B: Episode-like*

Elevated levels of particulate matter were measured during the first day of the period (Figure 6). During the remainder the measured PM10 levels do not significantly differ from the levels during the control periods. The size distribution for two selected hours is given in Figure 7. The period averaged contribution of PM$_{1_{\text{calc}}}$ and PM$_{2.5_{\text{calc}}}$ to PM$_{10_{\text{calc}}}$ is 18 and 27%. The maximum contribution of PM$_{1_{\text{calc}}}$ to PM$_{10_{\text{calc}}}$ occurred during the early nighttime hours of the first day (*cheaphour* 843) whereas the contribution of PM$_{2.5_{\text{calc}}}$ to PM$_{10_{\text{calc}}}$ reached its maximum at the same time PM10 itself peaked (during the late nighttime hours; *cheaphour* 849). This suggests that PM1 is not simply proportional to PM2.5 or PM10.

*Period C and D: Strong winds*

At the project sites PM10 levels measured during the first period (C) were no different from the control periods (Figure 8). However, the PM1 level was high (average 11.6 µg m$^{-3}$) and accounted for on average 28% of the calculated level of PM10, with a maximum of 37%. This lasted several hours after which it remained constant at 28%. The calculated PM10 level varied in that time between 8 and 43 µg m$^{-3}$. During period D (high winds) the PM10 concentration increased and the contribution of PM1 decreased (Figure 9).

All these observations seem to suggest that the extreme PM10 concentrations are caused by resuspended dust when the wind speed exceeds a threshold of about 10 m s$^{-1}$. In Figures 10 and 11 the size distribution measured during both periods is given, illustrating the differences. The low temperature (average -3.6 °C) and the concurring low relative humidity during period D (56 and 64% at the urban and rural sites, respectively) are favourable conditions for this phenomenon. Furthermore, the low to moderate levels of other air pollutants support the conclusion that the particulate matter originates from another source than from the ones active during period B and E, and is most probably resuspended dust. This is in agreement with the findings of Bloemen et al. (1995b) where low relative humidities and high wind speeds result in high PM10 levels.
**Period E: Pseudo-episode**

Period E can be marked 'pseudo-episode' as it lasted five days (all the weekdays from Monday to Friday) with pollutant levels that remained relatively high throughout the period. The concentrations are, however, below the levels that would mark it as a real episode. The PM10 concentration profile shows a clear diurnal pattern with raised levels during the night (Figure 12). The contributions of PM1 and PM2.5 remain constant over the period at 20 and 23% respectively, (Figure 13). The particle-size distribution is given in Figure 14.

The chemical speciation of the particulate matter is different from the previous two periods, as indicated by the levels of components like soot and, in particular, secondary aerosol (see Table 6 and Appendix A3).

**Table 6: Phenomenology of PM10 at the urban site (period averaged):**

1) contribution of PM1$_{\text{calc}}$ and PM2.5$_{\text{calc}}$ to PM10$_{\text{calc}}$, and

2) contribution of secondary aerosol (< 2.5 μm) and soot to PM10$_{\text{mean}}$

<table>
<thead>
<tr>
<th>Period</th>
<th>PM1 (%)</th>
<th>PM2.5 (%)</th>
<th>Secondary aerosol (%)</th>
<th>Soot (mV soot / μg m$^{-3}$ PM10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0a</td>
<td>9</td>
<td>21</td>
<td>19</td>
<td>93</td>
</tr>
<tr>
<td>0b</td>
<td>13</td>
<td>31</td>
<td>7</td>
<td>43</td>
</tr>
<tr>
<td>A</td>
<td>11</td>
<td>24</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>18</td>
<td>27</td>
<td>77</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>28</td>
<td>36</td>
<td>80</td>
<td>55</td>
</tr>
<tr>
<td>D</td>
<td>13</td>
<td>18</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td>E</td>
<td>20</td>
<td>23</td>
<td>66</td>
<td>56</td>
</tr>
</tbody>
</table>

Focusing on stagnant winter-type episodes, the following suggestions seem appropriate when taking into account a rather large uncertainty margin:

- The episode-like period B and the pseudo-episode period E show an increasing contribution of PM1 to PM10 (of a factor of 2, from circa 10 to 20% relative to the control periods). Apparently, PM1 does not contribute significantly to PM10 episode levels (on a mass basis). At the same time the PM2.5 fraction does not change significantly (= 25%).

- During stagnant episodes (B and E) the contribution of secondary aerosol is definitively increased to well over 65%, clearly dominating the observed PM10 episode levels. The apparent contradiction between the contributions of PM2.5 (23%) and secondary aerosol (66%) to PM10 was not yet resolved at the time of writing.
- The soot component is increased only marginally. Note in this respect that the soot measurement method employed only allows for the determination of fine-particle soot. Furthermore, traffic-related soot is mainly confined to the submicron particle range; hence, like PM1 it does not contribute significantly to the mass of PM10.
- Low PM10 levels do not always concur with other air pollutant components being low as well. For instance, during the control period 0a, low PM10 concentrations were observed, but high CO, NO, and soot levels point to a very local (traffic) source (e.g. unloading diesel vehicles in the immediate vicinity of the monitoring station). Apparently, appropriate control periods are poorly defined with only low PM10 levels.

4.2.2. Indicators
Benzene, CO and acetylene are acknowledged as traffic emission indicators.
In cities benzene is mainly emitted by mobile sources (Bloemen and Burn, 1993), allowing benzene to be treated as an indicator for traffic emissions. In Figure 15 the plotted average period concentrations of PM1 vs. benzene show a good correlation. Again the control period 0a proved to be an outlier. The benzene background level derived from this plot agrees with the level found at the rural site (2.0 μg m⁻³).
Unlike the period-averaged values, the hourly averages of benzene and PM1 showed less correlation, resulting partially from a different temporal variation during the day.
Benzene and CO are closely correlated when measured near to the emission source traffic. Figure 16 shows the average period concentrations of PM1 vs. CO.
It is known that the correlation of CO with benzene vanishes with distance from the source, explaining the (slightly) lower correlation of PM1 and CO compared with the correlation of PM1 and benzene for a city-background location (Aben et al., 1993).

Another compound related to benzene and its source is acetylene. The regression of PM1 on acetylene is similar to that of benzene:

\[ PM1 = 8.6 \times \text{acetylene} - 22.4 \ (R^2 = 0.95) \]
Comparing benzene and CO, the former has the advantage of being emitted by fewer sources than CO and the disadvantage of being less stable under atmospheric conditions. The regression of PM1 on benzene might open the possibility of estimating retrospectively PM1 levels using daily averaged benzene levels. An important constraint for generalizing the regression is the uncertainty of the spatial variation of the regression. Further investigation on this issue will be required.
4.2.3. Source apportionment

Source apportionment requires information about the composition of the emission. The observed concentrations of a multitude of compounds can be interpreted as the combination of the (dispersed, diluted and chemically transformed) emitted mixtures.

Applying principal component analysis (PCA) to obtain information on the profile of sources is based on the assumption that the variation of the concentrations of components is caused by varying emission strength of the various sources and simultaneous dilution due to atmospheric dispersion processes. Chemical and or physical reactions might modify concentrations, causing time to become a factor complicating the analysis. The PCA approach uses no chemical or physical constraints as do Chemical Mass Balance methods. The lack of appropriate source signatures renders the latter approach impossible.

An equal number of components and samples is a minimum mathematical condition; using three times the number of samples is optimal to arriving at reliable outcomes. This last condition is not fully met in most of the cases described from now on and the results should be interpreted with caution. The correlation matrix is used for the principal component analysis.

PCA was applied to the following set of components: particulate matter, particle-bound elements, PAHs and VVOCs.

Particulate matter

PCA using the parameters, soot (aethalometer signal), PAH (PAH-monitor signal), SO$_2$, CO, NO$_x$, the mass of the ultra fine particles calculated with the SMPS data (maximum size 0.8 μm) and the PM1 fraction calculated from the APS data revealed that 76% of the variance of the observed air pollution levels in a city background are determined by traffic-related emissions.

Elements

The PCA approach also included those samples collected at other times than the selected periods. The approximately 2:1 ratio of samples to elements restricted the impact of this approach. The results of the Amsterdam and Biddinghuizen sites were treated separately. Both data sets give a first principal component (PC) explaining one third of the variation and consist of nearly the same elements, including Pb, Al, Zn, Mn, V, I and Cd. For the rural site Cr and Se were added; Sn, on the other hand, is an element of the urban principal component.
PAHs
The number of PAH samples does not allow separate treatment of the data sets of each monitoring site. The PCA of all 18 samples shows a first PC, explaining 60% of the total variation and consists of the following PAHs: fluoranthene, pyrene, chrysene, benzo(a)fluoranthene, benzo(c)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and 11H-benzo(a)fluorene. Again, the impact of the PCA is moderate as the ratio of samples and compounds is approximately two.

(V)VOCs
VOCs were measured in a large number of samples and hence a separate PCA can be applied. As to the VOC data set, the ratio of samples and compounds is approximately 1.5; hence, the impact of the PCA low. Using these VOC data, two PCs explaining 63% of the variation are obtained. The first PC (48%) of the urban site consisted mainly of benzene and mono- to tri-alkyl aromatic hydrocarbons and cyclohexane, 2-methylhexane and C9-C11 alkanes. These compounds are mainly traffic-related. The second PC (15%) consisted of methylcyclohexane, cyclohexane and tetrachloroethene, compounds frequently applied as solvents. The corresponding first PC of the Biddinghuizen set, explaining 56% of the variation, showed a very strong correlation with the first Amsterdam PC ($R^2 = 99\%$).

VOCs were measured in 1200 (Amsterdam) and 1700 (Biddinghuizen) samples. The ratio of samples to compounds is more than 25, providing a reliable analysis. Two PCs explain 71% (48 and 23%) of the data set for the urban site. For the Biddinghuizen site one PC explains 56% of the variation. Similar to the VOC PCs, the first PC of both sites show a high correlation ($R^2 = 92\%$). Table 7 presents the compounds with high loadings on the PCs. These compounds can be considered to originate from a common source. PC A1 can be associated with traffic emissions as it contains benzene and acetylene. The fraction of the variation of PC1 illustrates the relevance of traffic emissions. Although PC B1 is strongly correlated with A1, it also contains compounds belonging to the second PC of the Amsterdam site (A2). This might be explained by the effect that the variation of the concentrations at the rural site is mainly caused by the rate of transport of air masses being polluted over an urban area.

The source characterizations given in this section might prove useful in identifying the sources of air pollution in cities. To quantify the impact of various emission sources is beyond the scope of this research.
Table 7: VVOCs of the first principal components
(A1, A2: first and second PC urban sites; B1: first PC rural site)

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>A2</th>
<th>B1</th>
<th>A1</th>
<th>A2</th>
<th>B1</th>
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<tbody>
<tr>
<td>acetylene</td>
<td>+</td>
<td></td>
<td>cis-2-pentene</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethane</td>
<td>+</td>
<td>+</td>
<td>cyclopentene</td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>ethene</td>
<td>+</td>
<td></td>
<td>i-pentane</td>
<td></td>
<td>+</td>
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</tr>
<tr>
<td>methyl acetylene</td>
<td>+</td>
<td></td>
<td>i-pentene</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>propene</td>
<td>+</td>
<td></td>
<td>n-pentane</td>
<td></td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1-butane</td>
<td>+</td>
<td></td>
<td>trans-2-pentene</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-butene</td>
<td>+</td>
<td>+</td>
<td>1-hexene</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>+</td>
<td></td>
<td>2-methylpentane</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>+</td>
<td>+</td>
<td>3-methylpentane</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-butane</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>benzene</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>i-butene</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>cyclohexane</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>methylcyclopentane</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>1-pentene</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>n-hexane</td>
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</tr>
<tr>
<td>2-methyl-1-butene</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>n-heptane</td>
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</tr>
<tr>
<td>2-methyl-2-butene</td>
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<td>+</td>
<td>toluene</td>
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<td>3-methyl-1-butene</td>
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<td>+</td>
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<td>ethylbenzene</td>
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<td></td>
<td>n-octane</td>
<td>+</td>
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<td></td>
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<td></td>
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<td>xylenes</td>
<td>+</td>
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<td></td>
<td></td>
<td></td>
<td>1.2.3-trimethylbenzene</td>
<td>+</td>
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</tr>
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<td></td>
<td></td>
<td>1.2.4-trimethylbenzene</td>
<td>+</td>
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</table>
5. CONCLUSIONS

The present study was designed to give a phenomenological description of air pollution in cities during winter-type smog episodes. However, no atmospheric conditions led to such an episode. Nevertheless, the results allowed the identification of five periods showing increased levels of particulate matter (PM10) and two periods with relatively low levels. Because this parameter is widely suspected to be associated with these effects, PM10 is commonly used as guidance parameter.

The results indicate that at least two different conditions lead to increased levels of particulate matter: (i) high winds, causing resuspension of settled dust, and (ii) stagnant weather conditions, with low rates of pollutant transport from the urban area. The first condition (wind speed over circa 10 m s\(^{-1}\)) leads to a significant increase of total suspended particulate matter (with a substantial mass of particles with a diameter up to circa 30 μm) due to resuspension. The size partitioning of the PM10 was not significantly different from the partitioning encountered during background situations. These conditions of high winds are scarcely encountered throughout the year. Hence, the effect on yearly averaged PM10 levels are thought to be marginal. The second condition causes increased air pollution levels of fine particles, originating from the transformation of gas-phase species to aerosols (for instance SO\(_2\) → SO\(_4\). During the project period these stagnant conditions occurred twice, resulting in minor to moderate air pollution levels.

During stagnant winter-type episodes the contribution (on a mass basis) of PM1 to PM10 is doubled from some 10 to 20%. At the same time the contribution of the PM2.5 fraction does not change significantly (circa 25% relative to PM10). The observed PM10 levels during stagnant episodes are clearly dominated by the secondary aerosol; its contribution to PM10 is increased to more than some 65%. The soot concentration did not increase significantly.

The good correlation between the PM1 levels and the compounds emitted by mobile sources suggests that traffic is the main source for PM1. Also the Principal Components Analysis applied confirms the dominating contribution of the traffic-related particulate matter to PM1.

Hence, both inside and outside episodes the traffic-related matter (e.g. soot) contributes only slightly to the mass of PM10, in realistic agreement with the aforementioned slight difference between PM10 levels observed in rural and urban areas. Consequently, a decrease in PM10 does not necessarily imply a proportionate decrease in traffic-related particulate matter, and vice versa.
The observed regression of PM1 on benzene might prove useful to estimating levels of PM1 over a longer time interval than the project period and for more sites. The advantage of selecting a commonly measured compound such as benzene for this purpose is the possibility for assessing exposure retrospectively. The regression needs to be treated with caution as the calibration of the particle sizer was not optimal for the finer fraction. Measuring simultaneously benzene and the particle-size distribution at various sites will be needed to confirm and refine this outcome. In this respect, size distribution measurements at the rural site were sadly lacking.

No real episode occurred during the project period. In fact, a real episode has become rare in recent years. However, another type of period with a high level of air pollution, New Year’s Eve, proved to be the most punctual. The concentrations of fine and coarse particulate matter are high but only for a rather short period. It is thought that these levels contribute, but only marginally, to cumulative exposure.
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Figure 1: VOCCARE2 located at the urban site of Amsterdam

Figure 2: VOCCARE1 located at the rural site of Biddinghuizen
Figure 3: PM levels during project period at the urban Amsterdam site
Figure 4: Measured PM10 levels vs. wind speed during periods C and D at the rural NAQMN stations in north-east part of the Netherlands.

Figure 5: Particle size distribution of 2 selected hours during period Oa.
Figure 6: Measured and calculated PM10 levels during period B.

Figure 7: Particle size distribution of two selected hours during period B.
Figure 8: Measured and calculated levels of PM10 at the urban Amsterdam site during period C and D.

Figure 9: Contributions of PM1 and PM2.5 to PM10 during period C and D.
Figure 10: Particle size distribution during selected hours of period C.

Figure 11: Particle size distribution during selected hours of period D.
Figure 12: Measured and calculated levels of PM10 during period E.

Figure 13: Contribution of PM1 and PM2.5 to PM10 during period E.

Figure 14: Particle size distribution during two selected hours of period E.
Figure 15: Regression of averaged benzene concentrations with averaged PM1 levels.

Figure 16: Regression of averaged CO concentrations with averaged PM1 levels.
### Appendix A1: Average concentrations at the urban (Ams) and rural (Bid) sites

<table>
<thead>
<tr>
<th>Component</th>
<th>Control periods</th>
<th>Fire works</th>
<th>Episode like</th>
<th>High wind speeds</th>
<th>Pseudo episode</th>
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<tr>
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<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
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<tr>
<td>CO (ppm)</td>
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<td>0.7</td>
<td>0.6</td>
<td>0.9</td>
<td>0.4</td>
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<tr>
<td>NOx (ppb)</td>
<td>109</td>
<td>51</td>
<td>177</td>
<td>13</td>
<td>62</td>
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<tr>
<td>SO2 (ppb)</td>
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<td>3</td>
<td>10</td>
<td>1</td>
<td>2</td>
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<tr>
<td>Temp (°C)</td>
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<td>0</td>
<td>4</td>
<td>-2</td>
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<tr>
<td>RH (%)</td>
<td>84</td>
<td>65</td>
<td>92</td>
<td>90</td>
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<td>94</td>
<td>85</td>
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### Appendix A2: Average concentrations at the urban (Ams) and rural (Bid) sites

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<th>Pseudo episode</th>
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<td>0a</td>
<td>0a</td>
<td>0b</td>
<td>0b</td>
<td>A</td>
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<tr>
<td>Soot (mV)</td>
<td>20</td>
<td>7 - 40</td>
<td>-</td>
<td>10</td>
<td>4 - 17</td>
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<tr>
<td>PAH (mV)</td>
<td>33</td>
<td>15 - 81</td>
<td>20</td>
<td>10</td>
<td>5 - 19</td>
</tr>
<tr>
<td>total PAH (ng/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benz(a)pyrene (ng/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benz(e)pyrene (ng/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fluoranthene (ng/m³)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pyrene (ng/m³)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chrysene (ng/m³)</td>
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<td>-</td>
<td>-</td>
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### Appendix A3: Average concentrations at the urban (Ams) and rural (Bid) sites

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<th>High winds</th>
<th>Pseudo episode</th>
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<td>0a</td>
<td>0b</td>
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</tr>
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<td><strong>component</strong></td>
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<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E</td>
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<td><strong>PM10_{observed}</strong></td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
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<td>8 - 34</td>
<td>16</td>
<td>-</td>
<td>36</td>
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<tr>
<td>PM10_{corrected}</td>
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<td>2 - 8</td>
<td>5</td>
<td>0 - 10</td>
<td>5</td>
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<tr>
<td>PM1</td>
<td>2</td>
<td>1 - 3</td>
<td>2</td>
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<td>PM10 / PM10</td>
<td>21</td>
<td>9</td>
<td>13</td>
<td>-</td>
<td>24</td>
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<td>PM10 / PM10</td>
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<td>22</td>
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<td>22</td>
<td>-</td>
<td>22</td>
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<td>Secondary aerosol</td>
<td>4</td>
<td>9 / 6</td>
<td>1 / 2</td>
<td>-</td>
<td>16 / 28</td>
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### Appendix A4: Average concentrations at the urban (Ams) and rural (Bid) sites

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<tr>
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<td>Aa</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
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<td>Benzene (VOC)</td>
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<td>Bid</td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
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<tr>
<td>6.6</td>
<td>2.1</td>
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<tr>
<td>3.1</td>
<td>1.3</td>
<td>7.1</td>
<td>1.6</td>
<td>-</td>
<td>17</td>
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<tr>
<td>2.9 - 3.3</td>
<td>1.2 - 1.4</td>
<td>5.6 - 8.6</td>
<td>1.1 - 2.2</td>
<td>-</td>
<td>0.5 - 4</td>
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<tr>
<td>Benzene (VOC)</td>
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<td>5.2</td>
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<td>1.9</td>
<td>4.5</td>
<td>3</td>
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<td>0.8 - 8</td>
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<td>2 - 4</td>
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<td>5 - 15</td>
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<td>2 - 4</td>
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<td>Toluene (VOC)</td>
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<td>-</td>
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<td>35</td>
<td>27 - 28</td>
<td>3.5</td>
<td>5</td>
<td>2</td>
<td>9</td>
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<td>28</td>
<td>5 - 13</td>
<td>3 - 4</td>
<td>2 - 7</td>
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<td>27 - 28</td>
<td>2 - 7</td>
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<td>2 - 4</td>
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<td>Toluene (VOC)</td>
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<td>12</td>
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<td>4</td>
<td>1 - 21</td>
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<tr>
<td>BTEX (VOC)</td>
<td>14</td>
<td>10</td>
<td>-</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>19</td>
<td>7</td>
<td>3 - 13</td>
<td>9</td>
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<td>4 - 34</td>
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<tr>
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<td>7 - 45</td>
<td>5 - 22</td>
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<td>4 - 20</td>
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<td>ΣC6 - C9 (VOC)</td>
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<td>20</td>
<td>1.1</td>
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<td>1.1</td>
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<td>0.5 - 3.5</td>
<td>1.4 - 4</td>
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## Appendix A5: Average concentrations at the urban (Ams) and rural (Bid) sites

<table>
<thead>
<tr>
<th>Component</th>
<th>Control periods</th>
<th>Fire works</th>
<th>Episode-like</th>
<th>High winds</th>
<th>Pseudo episode</th>
</tr>
</thead>
<tbody>
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<td>0b</td>
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<td>0.6</td>
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<td>0.15</td>
<td>0.1</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Tetrachloroethene (VOC)</td>
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<td>0.45</td>
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<tr>
<td>Component</td>
<td>Fireworks</td>
<td>Episode-like</td>
<td>High winds</td>
<td>Pseudo episode</td>
<td></td>
</tr>
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<td>-----------</td>
<td>--------------</td>
<td>------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
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<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
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</table>

Average concentrations at the urban (Ams) and rural (Bld) sites.
### Appendix A7: Average concentrations at the urban (Ams) and rural (Bid) sites

<table>
<thead>
<tr>
<th>Component (µg/m³)</th>
<th>Control periods</th>
<th>Fireworks</th>
<th>Episode like</th>
<th>High winds</th>
<th>Pseudo episode</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>0a</td>
<td>0a</td>
<td>0b</td>
<td>0b</td>
<td>A</td>
</tr>
<tr>
<td>Al</td>
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<td>0.96</td>
<td>0.44</td>
<td>0.31</td>
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<tr>
<td>B</td>
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<td>0.05</td>
<td>0.013</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Ba</td>
<td>0.12</td>
<td>0.16</td>
<td>0.56</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>Cd</td>
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<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
<td>0.002</td>
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<tr>
<td>Ce</td>
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<td>0.005</td>
<td>0.002</td>
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<td>0.001</td>
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<tr>
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<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td>Cu</td>
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<td>0.12</td>
<td>0.07</td>
<td>0.60</td>
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<tr>
<td>I</td>
<td>0.004</td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
<td>0.002</td>
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<tr>
<td>Li</td>
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<td>0.007</td>
<td>0.006</td>
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<td>0.005</td>
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<tr>
<td>Mg</td>
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<td>Ni</td>
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<td>0.32</td>
<td>0.22</td>
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<tr>
<td>Pb</td>
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<td>0.07</td>
<td>0.03</td>
<td>0.10</td>
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<tr>
<td>Se</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
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<td>0.004</td>
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<td>0.05</td>
<td>0.023</td>
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<tr>
<td>Zn</td>
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<td>0.09</td>
<td>0.18</td>
<td>0.07</td>
<td>0.26</td>
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</table>
Appendix A8: Average concentrations at the urban (Ams) and rural (Bid) sites

<table>
<thead>
<tr>
<th>Component (µg/m³)</th>
<th>Control periods</th>
<th>Fire works</th>
<th>Episode like</th>
<th>High winds</th>
<th>Pseudo episode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0a</td>
<td>0a</td>
<td>0b</td>
<td>0b</td>
<td>A</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
<td>Bid</td>
<td>Ams</td>
</tr>
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<td></td>
<td>10.1</td>
<td>7.7</td>
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<td>-</td>
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<tr>
<td>Acetaldehyde</td>
<td>69.5</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>
Appendix B:

Procedure to calculate SPM levels from observed particle size distributions

B.0 Introduction

The annex describes the computational procedure to calculate PM10 from observed particle size distributions, and the sampling convention from ISO7708 (van der Meulen, 1986).

B.1 Nomenclature

- $E_t$: particle size dependent inhalable sampling convention
- $E_T$: particle size dependent thoracic sampling convention
- prob: cumulative lognormal distribution as function of particle diameter, i.e.
  \[
  \text{prob}(D, D_{50}, \sigma) = \int_{x_{\text{min}}}^{D} \frac{dx}{x} \cdot \frac{1}{\sqrt{2\pi} \cdot \sigma} \cdot \exp\left\{ -\frac{\ln(x/D_{50})^2}{2 \cdot \sigma^2} \right\}
  \]
- $D_{50}$: 50% cutoff aerodynamic diameter
- $\sigma$: geometric standard deviation
- $D$: aerodynamic particle diameter (μm)
- M(D): ambient particle size distribution, as measured by SMPS/APS
- <PM10>: calculated PM10 level
- $U$: windspeed (m/s)

B.2 Thoracic fraction

ISO7708 gives definitions for the following fractions of SPM: inhalable fraction, thoracic fraction, and respirable fraction. These fractions comprise the mass fractions of particles (as a percentage of SPM) which penetrate to specified regions of the respiratory tract.

The inhalable fraction is defined as the mass fraction of SPM which is inhaled through the nose and mouth. This fraction depends mainly on the speed and direction of the wind, and breathing rate and breath volume. ISO expresses the inhalable sampling convention, when averaged over all wind directions, as follows:

\[
E_t = 50 \cdot (1 + \exp[-0.06D]) + 10^{-3} \cdot U^{2.75} \cdot \exp[0.055D] \text{ (\%)}
\]

where $D$ is expressed in μm, and $U$ in m/s.

Basically, this formulae does not imply any effective upper cutoff diameter. Experimental data on the inhalable fraction do not (yet) exist for $D > 90$ μm and $U > 9$ m/s. Hence, application of the convention should be limited to the domain $D < 90$ μm and $U < 9$ m/s.
The thoracic fraction is defined as the mass fraction of inhaled particles which penetrates beyond the larynx. The thoracic sampling convention is expressed as a filter function with respect to SPM:

$$E_T = E_f \times (1 - \text{prob}(D, D_{50}, \sigma))$$

with: $D_{50} = 50\%$ cutoff diameter with respect to the inhalable fraction.

Following the ISO 7708 convention: $D_{50} = 11.64 \mu m$ and pertinent geometric standard deviation $\sigma = 1.5$. This implies an effective $50 \%$ cutoff diameter with respect to SPM: $D_{50} = 10 \mu m$; accordingly, the upper cutoff amounts to some $30 \mu m$.

### B.3 Calculation of PM10

Starting from the thoracic (PM10) sampling convention $E_T$ and the ambient particle size distribution $M(D)$, the calculated PM10 level follows as:

$$<\text{PM10}> = \int M(D)E_TdD$$

As can be inferred from the ISO thoracic convention, the fine particles below some $5 \mu m$ are virtually sampled with unit efficiency. Hence PM1 an PM2.5 follow straightforwardly as:

$$<\text{PM2.5}> \text{ or } <\text{PM1}> = \int M(D)dD,$$

with the upper limit of integration extending to 2.5 or 1 $\mu m$ respectively.