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Anthropogenic and natural constituents in particulate matter in the Netherlands

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Abstract

To develop mitigation strategies for reducing concentrations of both $PM_{2.5}$ (and PM_{10}), the origin of particulate matter (PM) needs to be established. An intensive, one-year measurement campaign from August 2007 to August 2008 was carried out to determine the composition of PM_{10} and $PM_{2.5}$ at five locations in the Netherlands, aiming at reducing the uncertainties on the origin of PM. Generally, a considerable conformity in the chemical composition of $PM_{2.5}$ (and PM_{10}) was observed. From all the constituents present in $PM_{2.5}$, the secondary inorganic aerosol is the most dominant (42–48%), followed by total carbonaceous matter (22–37%). Contributions due to sea salt (maximum 8%), mineral dust and metals (maximum 5%) are relatively low. For the first time, a detailed overview can be presented of the composition of the coarse fraction. Compared to the fine fraction, contributions of the sea salt, mineral dust and metals are now larger resulting in a more balanced distribution between the various constituents. Through mass closure a considerable part of the PM mass could be defined ($PM_{2.5}$: 80–94%). The chemical distribution on days with high PM levels showed a distinct increase of nitrate as well as in the mass not accounted for. Contributions of the remaining constituents remained equal of were lower (sea salt) when expressed in percentages. A correspondence between nitrate and the unknown mass was observed hinting at the presence of water on the filters. The contribution from natural sources in the Netherlands was estimated to be about 25% for PM_{10} and 20% for $PM_{2.5}$.

1 Introduction

Although air quality in Europe has improved substantially over the past decades, air pollution still poses a significant threat to human health (EEA, 2007). Health effects of air pollution are dominated by particulate matter, both $PM_{2.5}$ and PM_{10}. Short-term exposure to PM has frequently been associated with increased human morbidity and mortality (e.g., Brunekreef and Holgate, 2002). Effects of long-term exposure to PM are much more uncertain than the short-term effects, but are believed to have a much greater effect on health loss (Dockery et al., 1993; Pope et al., 1995). Recent estimates arrive at an average loss of life expectancy of about 6–12 months in the Netherlands (EEA, 2007). So far, there is no conclusive evidence which component or components are most relevant for deteriorating human health, although some suggestions have been made, e.g. soot (Hoek et al., 2002). Therefore, the European air quality standards currently focus on PM_{10} and $PM_{2.5}$.

At present, many countries in Europe, including the Netherlands, have problems adhering to the daily limit value for PM_{10} at hotspot locations. In the Directive (2008/50/EC) on ambient air quality and cleaner air for Europe (EU, 2008) new air quality standards for fine particulate matter ($PM_{2.5}$) have been established. An annual mean $PM_{2.5}$ concentration of 25 µg m^{-3} has been set as target value to be achieved in 2010 and as limit value to be adhered to by 2015. The new directive introduces additional $PM_{2.5}$ objectives, that aim to a reduce human exposure to $PM_{2.5}$. The average exposure indicator (AEI) is a three-year averaged $PM_{2.5}$ level measured at urban background locations throughout European Member States. A reduction target of 15% of the AEI between 2010 and 2020 for the Netherlands might be reached under current legislation, whereas a reduction of 20% is probably not even reached with outlined additional measures (Matthijsen et al., 2009). To develop mitigation strategies to meet these targets and to reduce the concentrations of both $PM_{2.5}$ and PM_{10} in general one needs to establish the origin of particulate matter. Of particular interest is the quantification of the anthropogenic and natural fractions in PM as these provide an indication of the "playing field" of policy makers.

Important information on the origin of particulate matter can be obtained through chemical analysis to establish its composition (Putaud et al., 2004, 2009; Viana et al., 2008; Sillanpää et al., 2006; Salvador et al., 2007; Mazzei et al., 2008; Almeida et al., 2007). Many components can be used as tracers for specific sources. For example, sodium is a tracer that is almost exclusively associated with sea salt. However, one is usually not able to analyze the full composition and a significant portion of the particulate mass is therefore unknown. Using assumptions on the relationships between (a group of) tracers and major constituents one can attribute the mass to these constituents, the so-called chemical mass balance (CMB) approach (Harrison et al., 2003). In this way an estimate can be derived for the major source contributions to PM. Though CMB significantly reduces the unknown mass a total mass closure is usually not attained. The (relative) magnitude of the unexplained mass is an indicator for the uncertainty in the mass attribution. To independently address such issues one can apply statistical techniques to the observation dataset to address the possible source categories for PM. Techniques such as positive matrix factorization (PMF) can be used to search for groups of components with the same behaviour in time, which are then assumed to derive from a single source or group of similar sources (Hopke et al., 2001). Hence, a mass closure approach as well as PMF will give us independent insights from an empirical point of view in the actual PM sources.

Here, a mass closure approach is used to study the chemical composition of PM_{10} and $PM_{2.5}$ filter samples that were collected in the Netherlands at five measurement sites for a period of one year. The study was executed within the framework of the Policy-Oriented Research Program (BOP) and described in detail by Schaap et al. (2010). The general aim of this national program was to reduce knowledge gaps about composition, distribution and origin of particulate matter in the Netherlands. This study established the chemical composition measured at Dutch rural and urban locations. Properties of various constituents in fine and coarse matter, respective mass deficits and the changing composition on days with higher PM masses are demonstrated. Also, the contribution of natural material in particulate matter and political implications are discussed. The usefulness of the PMF approach is demonstrated elsewhere (Mooibroek et al., 2010; Schaap et al., 2010) who applied this technique on the same data set.

2 Experimental methods

2.1 Monitoring locations

Five sites were selected for the monitoring of the PM_{10} and $PM_{2.5}$ composition (see Fig. 1). These include three rural background sites: Hellendoorn (~ 150 km from Rotterdam), Cabauw (~ 50 km from Rotterdam) and Vredepeel (~ 100 km from Rotterdam). Cabauw represents the rural background for the (industrialised) western part of the country whereas Hellendoorn and Vredepeel were selected to add information from the eastern and southern parts where agriculture dominates. At Vredepeel intensive livestock activity exists in the direct surroundings. Like to the rural sites, the urban background location Schiedam belongs to the Dutch National Air Quality Monitoring Network (NAQMN) maintained by RIVM. The kerbside (traffic) site in Rotterdam is part of the regional air quality network operated by DCMR. Further characteristics of the locations are given in Table 1.

2.2 Measurement strategy

The filter collection routine (PM_{10} and $PM_{2.5}$) took place every second day between 15 August 2007 and 4 September 2008. Chemical analysis was done every fourth day. For each of the five sites the following components in the filter samples were determined: sodium, chloride, sulphate, nitrate, ammonium, organic carbon, elemental carbon and metals (and silicon). The filters were collected according to the reference method described in the European Standards (EN12341: 1998 and EN14907: 2005). The measurement instrument was the SEQ47/50 (Leckel GmbH, Germany). In the BOP programme's experimental set-up this sequential low-volume system (LVS) used a flow of $2.3\,m^3\,h^{-1}$. Four of these reference samplers were placed at every location for a paired measurement of PM_{10} and $PM_{2.5}$. The sampling period per filter is 24 h and ran from midnight to midnight. All filters were protected during storage and transport. The logistic and operational (QA/QC) procedures were those used in the NAQMN network.

Two types of filter media, quartz (QMA) and teflon (PTFE), were used. The teflon filters were chosen to quantify the presence of silicon. The quartz fibre filter media is the material commonly used in gravimetric studies. They were cut into two equal parts for the SIA and EC/OC analyses.

2.3 Chemical analyses

Ammonium captured on the filters was analysed on the AMFIA (AMmonia Flow Injection Analyser, a flow injection system built at ECN). The system is based on the selective diffusion of NH_4^+ at reduced pH by conductivity. The detection level is 0.2 µg per filter. Sulphate and nitrate were measured in aqueous solutions with the Dionex IC25. This system combines a Ion Chromatography System with a conductivity detector and a high performance dual-piston pump combined into one compact package. Samples were eluted through an ion-exchange column using a dilute sodium hydroxide solution. The eluent is passed through self-regenerating suppressors that neutralise the eluent conductance, ensuring that electrochemical detectors (conductivity or pulsed amperometric) can detect the ions down to sub-ppm concentrations. Detection level is 0.7 µg per filter.

The analysis of carbon is based on thermography (Cachier-method). The filter-sample is heated in an oven resulting in the release of carbon. For quantitative determination of the amount of released carbon the evolved gases are oxidised to CO_2 in a post-combustor oven. The discrimination of carbon in OC and EC is operationally defined. OC is the carbon released during the 1st step (8 min at 340 °C); the remainder gives an estimate for EC after combustion for 6 min at 750 °C. The analysis occurs in a Coulomat 702, manufactured by JUWE (Viersen, Germany). The total amount of carbon, TC, is directly proportional to the total amount of CO_2 produced. The detection system, in principle, is an absolute method. Monthly calibrations with a standard were performed. Cleaning of the instrument occurred once a month (after a full month of operation). Several samples were in the oven for a longer period and also at a higher temperature to check for complete combustion and proper assessment of the

EC. The lower detection limit of the method was around 5 µg per filter corresponding to a concentration of 0.1 µg m^{-3}. An average experimental blank of 1.2 µgOC m^{-3} was found during the campaign (ten Brink et al., 2009) consisting of a filter blank of 0.5 µg m^{-3}, and a field blank of 0.7 µg m^{-3} (due to gas adsorption on the filter material). As the latter contribution ordinarily occurs in routine PM determination following the reference method, we only subtracted the filter blank from the measured OC values.

ICP-MS was employed to analyse the elemental composition of the collected PM_{10} and $PM_{2.5}$ masses. In short, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) is capable of determining a range of metal and non-metal concentrations with high sensitivity. It is based on combining an inductively coupled plasma to produce ions with a mass spectrometer as a method of separating and detecting the ions. ICP-MS is a standard operational technique in NAQMN. In this study, we use the (summated) elemental mass primarily to estimate the contributions of suspended mineral dust and total metals.

2.4 Data handling

For each site only filter samples were included with a complete characterization. Completeness was interpreted rather strict: if one of the components were missing the entire sample was excluded. As a consequence, the number of samples at a site available for interpretation differ from site to site. The selected filter data lie within the period January–August 2008. The composition of the coarse fraction was obtained by subtracting the concentrations in the $PM_{2.5}$ sample from those in PM_{10} followed by the calculation of the averages and standard deviations. Next, the mass concentrations of all the components were summated and compared with the weighted mass to establish the “not-analysed” part (further denoted by “NA”). The sum of the measured elements (without sodium) is abbreviated as “total metals”.

3 Results

3.1 Chemical composition

The average PM concentrations in our data set are 22.1 µg m^{-3} (PM$_{10}$), 14.8 µg m^{-3} (PM$_{2.5}$) and 7.3 µg m^{-3} (PM$_{10-2.5}$) indicating that PM$_{2.5}$ is around two-third of PM$_{10}$ which is common in the Netherlands. As expected, levels appear highest at the Rotterdam kerbside and lowest at rural Hellendoorn. The mass difference for PM$_{10}$ between these sites is considerable (near 9 µg m^{-3}) and originating from nearly equal increments of the fine and coarse mass (4–5 µg m^{-3}).

The average composition of the daily PM$_{10}$ and PM$_{2.5}$ filter samples is presented in Fig. 2 and summarised in Table 2. An example of the compositional distribution can be seen in Fig. 3 (Schiedam). Figure 2 directly shows that similarity exists in the chemistry of PM at the various locations. The largest contributions come from nitrate. The concentrations of the NA part in the various fractions is at least of similar level. The only exception is, not unexpectedly, observed at the kerbside location (Rotterdam) where comparable quantities of carbon in the fine fraction and (summated) metals in the coarse fraction were found. This is explained by the emissions from traffic passing nearby. At the other sites the next important component in PM$_{2.5}$ (and PM$_{10}$) is sulphate, followed by elemental carbon, and, in various order, organic carbon, ammonium, metals, chloride and sodium. The major parts of the inorganic components, elementary and organic carbon, and NA are in the fine fraction. Contributions of metals and sea-salt related components (sodium and chloride) mainly arrived from the coarser-sized particles. Notable is further the spatial similarity of the nitrate and ammonium levels with those of the not-analysed part at the five sites. In particular, this is seen in the PM$_{2.5}$ data and suggests a common origin.

At the two urban sites (Schiedam and Rotterdam) nitrate appeared as one of the more important components within PM$_{10}$ with levels near or above 4 µg m^{-3}. Considerable part of this was in the coarse fraction (1.5 and 1.8 µg m^{-3}, respectively).

A similar pattern was seen for sulphate but with lower concentrations. Somewhat surprisingly, the highest nitrate, ammonium and sulphate concentrations occurred in the $PM_{2.5}$ mass collected at Cabauw. These were even higher than at Vredepeel which is a site known to be influenced by livestock activity. Although the rural location of Cabauw was less suspect in this respect, local emissions of ammonia cannot be excluded and it would explain the elevated concentrations. As a consequence, the assumption that Cabauw could serve as a background site for the urban region (containing the Rotterdam and Schiedam locations) is not confirmed.

The range of OC concentrations in PM_{10} is between 1.6 $\mu g\, m^{-3}$ (Hellendoorn, Cabauw) and 2.3 $\mu g\, m^{-3}$ (Rotterdam). A recent study by ten Brink et al. (2009) indicated that 70% of the OC in the Netherlands is contemporary (due to emissions from biogenic material and wood combustion). The remainder would originate from fossil-fuel sources (i.e. diesel traffic emissions). OC in the coarse fraction is highest at Vredepeel, Cabauw and Rotterdam (compared to Hellendoorn). At the first two sites this is probably related to nearby biogenic emissions nearby while at Rotterdam emissions are predominantly from vehicles.

3.2 Conversion formula used in the mass closure approach

Certain conversions were applied to the data set to identify the various constituents in PM. This procedure contained estimations of associated oxygen of metals, sea salt (SS), sea-salt sulphate (SS-sulphate), total carbonaceous matter (TCM) and mineral dust (MD). The outcome effectively reduces the “not-analysed” part into a “not-explained” or “unknown” part in the final mass closure. We shortly discuss here the impacts on the mass closure (summarised in Table 3).

Elemental concentrations have been recalculated to their respective oxides to account for associated oxygen. The summated “oxidised” contribution appeared 1.4 to 1.5 higher than the elemental contribution. Its incorporation had the largest effect on the coarse fraction: up to 1.0 µg m^{-3} (Rotterdam). The change in $PM_{2.5}$ was rather small (< 0.4 µg m^{-3}). Consequently, the mass closure improved most for the coarse fraction (9%, on average).

The sea-salt aerosol is generated by sea spray processes when waves break on the sea shore and out at sea. Here, sodium is used as a tracer because it is not affected by depletion and measurements are reliable. The presence of sea salt is then estimated by: SS = 3.26*Na (contribution Cl is then neglected). The factor 3.26 follows from the composition of sea water (i.e., 1 l sea water contains 1 g material among which 0.308 g sodium). The change in the not-analysed part is calculated with respect to the sum of Na and Cl (where minor contributions of magnesium and other components present in seawater were neglected). Generally, the application of the sea-salt conversion has a similar effect as the incorporation of oxidised elemental concentrations. Again the coarse fraction is affected most: the average sea-salt contribution rose with 0.7 µg m^{-3} which corresponds with an improvement of 10% in the mass closure. The sulphate concentrations have been corrected for a sea-salt contribution which is estimated by Na*(7.68/30.60). The ratio is determined by the molar weights of sulphate and sodium. The sea salt contributions in relation to sulphate appear rather low (< 0.3 µg m^{-3}). The sea salt contribution to the coarse fraction and the effect of Cl-depletion will be treated further in Sect. 4.3.

Carbonaceous constituents in PM contain other elements than carbon contributing to the mass of PM (e.g., oxygen). The conversion from OC to organic material (OM) is rather uncertain: in literature the factor varies between 1.2 and 2 and it may well be possible that the value decreases near emission sources and increases in aged air masses. US-EPA includes the associated elements in their approach by following Frank (2006) who compared total mass with summated contributions of components analysed for a very large number of filters. Frank calculated that total carbonaceous matter (TCM) defined by 1.3 times the amount of total carbon (TC) would have the best agreement. An additional reason to use total carbon and not convert OC to OM is due to the uncertain OC-EC split in the chemical analysis. Current analysis procedures correspond well for total carbon, but yield very different EC/OC ratios (ten Brink et al., 2009). Using the approach of Frank the largest relative change is calculated for $PM_{2.5}$ which is no surprise as TC is predominantly present in the fine fraction. The mass closure improved with some 7%. The maximum change was observed at the kerbside site in Rotterdam ($+1.4\,\mu g\,m^{-3}$).

Mineral dust is defined here as fugitive wind-blown and mechanically resuspended soil dust with a composition comparable to the earth's crust containing elements like Si, Al, Ca, K, Fe and Ti. In our data set the correlation between Al and Si turned out to be very good ($r^2 = 0.96$). This suggests that both originate from the same source and are present in similar ratios. The method to estimate the contribution of MD here is by focusing on these two abundant elements according to $MD = 0.49^{*}Si + (2.36^{*}Si + 2.7^{*}Al)$ (proposed by Denier van der Gon, 2009). All elemental weights were recalculated first to their respective oxide concentrations. The calculated MD contribution is subtracted from the total elemental mass which leaves the final mass balance unaffected.

3.3 Mass closure

The resulting concentrations of the various constituents are given in Table 4. The resulting mass closure is again given for the Schiedam site in Fig. 4. The dominant constituent in the $PM_{2.5}$ filter samples is the secondary inorganic components (SIA). There is not much difference between most measurement sites as concentrations range between 6 and $7\,\mu g\,m^{-3}$. A maximum occurs at Cabauw ($8.4\,\mu g\,m^{-3}$) due the enhanced levels of ammonium and nitrate noted earlier. The second important contribution comes from total carbonaceous matter (TCM) showing more variation. TCM in $PM_{2.5}$ is higher at the urban sites ($4.0–6.1\,\mu g\,m^{-3}$) than at the rural sites ($3.3–3.9\,\mu g\,m^{-3}$). The remaining constituents, i.e., sea salt (SS), mineral dust (MD), and metals contribute considerably less with concentrations always below $1\,\mu g\,m^{-3}$. The unexplained part in the $PM_{2.5}$ mass fraction tends to be higher at the rural sites with a maximum at Cabauw of 3.5 µg m^{-3}. At the other sites the missing part was always less than 2.5 µg m^{-3}.

The presence of the various constituents in the coarse fraction is more evenly distributed than in the fine fraction. Relatively high contributions arise from sea salt (≤ 2.7 µg m^{-3}; maximum at Schiedam) and SIA (≤ 2.3 µg m^{-3}; higher levels at Rotterdam and Schiedam). The concentrations of MD and the remaining metals are always less than 1.4 µg m^{-3} (Cabauw) and 1.6 µg m^{-3} (Rotterdam), respectively. Remarkable is rather high TC levels at Vredepeel (1.3 µg m^{-3}) and Cabauw (0.7 µg m^{-3}) compared to Rotterdam (1.2 µg m^{-3}) and Schiedam (0.7 µg m^{-3}) The reason for these enhanced TC levels in the coarse fraction is not clear.

To determine which of the constituents are the main contributors when high PM levels (e.g., on exceedence days) occur the data set has been partitioned into two subsets, containing the data for days at which the PM$_{10}$ (PM$_{2.5}$) concentrations were less or larger than 30 (25) µg m^{-3}. Not surprisingly, the absolute contributions of most constituents rise when PM increases. The difference between the PM$_{10}$ levels when averaged over the two sets is 20 µg m^{-3}. The largest changes in absolute concentrations are observed for SIA (+11 µg m^{-3} in PM$_{10}$) and the unknown part (+6 µg m^{-3}) followed by smaller or negligible changes for TCM (+3 µg m^{-3}), MD (+1.5 µg m^{-3}) and metals (< +0.5 µg m^{-3}). The only exception is sea salt which decreases at higher PM levels (–1.8 µg m^{-3}). The corresponding changes in chemical distributions of PM$_{10}$ and PM$_{2.5}$ are summarised in Fig. 5. It can be seen that when expressed in percentages both SIA and the unknown part become more dominant at days with more PM. Correspondingly, the relative contributions of the remaining constituents (MD, TCM and SS) decrease at higher PM concentrations.

The two measurement sites in the Rotterdam urban area allow investigating which components are emitted by traffic by comparing measured concentrations at the kerb site (Rotterdam) to those at the urban background site (Schiedam). The difference in PM$_{10}$ between the two sites appeared 3.5 µg m^{-3} (based on 27 corresponding days) and can be attributed to carbonaceous material (2.5 µg m^{-3}) and metals (1 µg m^{-3}).

The carbonaceous material increment is largely due to elementary carbon. The metals that are enhanced include copper, iron, barium and molybdenum and result from tailpipe emissions (TCM), and brake and tire wear. Surprisingly, there is no increment in the concentrations of mineral dust. This indicates that at Rotterdam resuspension is not a significant source disagreeing with the outcome from other studies (e.g., Amato et al., 2009).

4 Discussion

4.1 Chemical composition

The data set gives a proper insight in the chemical characteristics of PM in the Netherlands. Generally, a considerable similarity in the chemical composition of PM is observed at the five measurement sites. Always, secondary inorganic components are the dominant constituent with contributions responsible for nearly half of the total mass (42–48% of $PM_{2.5}$) with nitrate as the most important component. The variation in SIA concentrations appears rather limited indicating that its behaviour is mainly driven by larger-scale meteorology and not by local sources. Nearby emissions of ammonia may incidentally lead to locally high levels (e.g., Cabauw). The next important contribution originates from total carbonaceous matter showing more variation over the sites studied here (22–37%). TCM in $PM_{2.5}$ tends to be higher in areas where more traffic prevails (Rotterdam, Schiedam). The remaining constituents, i.e., sea salt, mineral dust and metals are relatively unimportant as they contribute each less than 8%.

The study allows the first detailed overview of the chemical composition of the coarse fraction in the Netherlands. Compared to the fine fraction both SIA and TCM are less dominant (around 29% and 25%, respectively) becoming comparable with mineral dust (<23%) and sea salt (<30%). The remaining metals sum up to 16% (Rotterdam). It was further noted that at the two urban sites considerable part of SIA (25%) was in the coarse fraction. It is assumed that in the marine urban environment (Schiedam and Rotterdam are within 30 km of the seashore) the coarse sea-salt particles act as reactive sinks for nitric and sulphuric acids. The implications of these mechanisms will be discussed further below.

As anticipated, absolute contributions of most constituents rise when PM concentrations go up. However, this does not occur at the same rate for each constituent. The largest increase is observed for SIA, most notably nitrate, and the missing mass part. By consequence, the chemical distribution rearranges at days with higher PM concentrations: SIA and the unknown part become more dominant, the contribution of mineral dust remains the same while the relative importance of TCM and sea salt decrease. Such behaviour can be explained by considering the atmospheric situation these days and the localisation of the major emissions. The high concentrations of $PM_{2.5}$ and PM_{10} occur at days with stagnating conditions or slow transport from south, south-east or east. As the emissions are diluted less due to the lower wind speeds and removal is low, pollution starts to build up. During the winter period this effect is strengthened due to the shallow boundary layers. In view of the dominant transport direction (continental) it is not surprising that the contribution of sea salt diminishes. In addition to unfavourable meteorological conditions, considerable emissions for SO_2 and NO_x take place east of the Netherlands (industrial Ruhr area); for NH_3 this is in the Southeast (a centre of intensive livestock industry). Model studies also indicate high contributions of national sources to the concentrations of primary material and ammonium nitrate (Schaap and Denier van der Gon, 2007). Also some special events contribute to a (small) number of exceedence or days with high concentrations. In the data set we have identified contributions from desert dust, fireworks at New Year's Eve, and bonfires at Easter.

4.2 Mass closure and the unknown part

To correct for known underestimations we applied a number of algorithms to estimate various constituents. Most of these recalculations (oxide concentrations, sea salt, total carbon material) improve the mass closure. For example, in case of $PM_{2.5}$ the conversion from TC to TCM results in a decrease in the unknown mass part of 6–8%. Not surprisingly, the more complete mass closure in the $PM_{2.5}$ samples was obtained at the urban sites (93–94%). The closure appears less perfect at the rural sites (80, 83 and 90%) demonstrating the sensitivity on site characteristics. As noted earlier, SIA do not largely differ in $PM_{2.5}$ (and PM_{10}) between the locations. As the contributions of the remaining components are relatively minor in $PM_{2.5}$, a larger contribution of TCM in $PM_{2.5}$ at urban locations results in a smaller part of PM that is unexplained.

In contrast to the fine fraction, the mass closure in the coarse fraction seems better at the rural sites. Here, the unexplained parts are less than 4% of the total mass (which is in absolute mass units negligible) while in the urban environment it is 12% (Rotterdam) and 16% (Schiedam) or, in absolute value, 1 and 1.5 $\mu g\, m^{-3}$, respectively.

A correlation is observed between the SIA presence in $PM_{2.5}$ (more specific, nitrate and, to a lesser extent, ammonium) and the amount of unexplained mass at the five sites. For example, the largest mass deficit (measured at Cabauw) coincides with the highest SIA concentration; at Schiedam minimum SIA concentrations and mass deficit have been measured. To a lesser extent, a similar behaviour is noted for the coarse mass fraction. Here, the SIA concentrations at the urban sites are (somewhat) higher corresponding with larger mass deficits. By consequence, also the "contribution" of the unexplained mass becomes more important at days with higher PM concentrations since the presence of SIA (or more specific nitrate) is the main reason for these augmented levels.

A possible reason may be the amount of water attached to SIA. Water is a natural component of particulate matter. Hygroscopic salts on particles, like ammonium nitrate and ammonium sulphate in the fine fraction, and sodium nitrate and sodium sulphate in the coarse fraction attract water. The water bound to particles contributes to the PM mass measurements. Ideally, this water is removed by pre-heating of the air sample or by conditioning of the filters under dry (50% RH) circumstances following the reference method (NEN12341). However, heating or drying only partly removes the particle bound water due to hysteresis (e.g., Speer et al., 2003). They report molar ratios between 0.5 and 1.0 for water on ammonium nitrate and ammonium sulphate particles at a RH of 50% and 75%, respectively. PM_{10} reference measurements are to be performed at temperature of 20 °C and a relative humidity of 50%. With a molar ratio of 0.5 for water on ammonium nitrate and ammonium sulphate particles. As such, we estimate the amount of water on PM_{10} due to the presence of SIA is about 10% of the SIA mass. This results in an estimate of 4–5% of the PM_{10} mass concentration. Such a contribution is possible as it is generally lower than the total unexplained mass. Concluding, water is expected to be an important, though not the sole, contributor to the unexplained mass.

A similar water uptake may be associated with sea salt. However, as the contribution of sea salt to the total mass is low, its water contribution is much less compared to that of SIA, at least in the case of $PM_{2.5}$. Likewise the amount of water on organic carbon (OC) is unlikely to play an important role. The contribution of hygroscopic OC to ambient PM levels in the Netherlands is much smaller than the contribution of SIA. Hygroscopic OC is a fraction of the total OC amount ($\sim 2\,\mu g\,m^{-3}$) and thus much lower than SIA levels ($\sim 10\,\mu g\,m^{-3}$). Moreover, the amount of water bound to a unit OC is less than on SIA (Speer et al., 2003).

4.3 Role of nitrate

According to the formation pathways ammonia gas reacts reversibly with HNO_3 to form its ammonium salt, NH_4NO_3, which is semi-volatile and may release their gas phase precursors under conditions of low atmospheric NH_3 levels or high temperature according to $NH_3 + HNO_3 \leftrightarrow NH_4NO_3$. In marine and coastal atmospheres, nitric acid is also converted into particulate nitrate ($NaNO_3$) through the reaction with sea salt particles resulting in the release of HCl: $NaCl + HNO_3 \rightarrow NaNO_3 + HCl$. In contrast to NH_4NO_3, $NaNO_3$ is a non-volatile compound under atmospheric conditions therefore, partitioning of nitric acid into the sea salt is irreversible. In the Netherlands most of the nitrate is found in the fine mode as ammonium nitrate. However, the coarse nitrate fraction is still a substantial part of the analysed coarse mode (Table 2). In particular, the coarse-to-PM_{10} ratio in the case of nitrate is near 40% at the urban sites (and some 26% at the rural sites).

It is this formation pathway that poses a complication in the chemical mass closure approach. In the chemical mass balance sodium is used as a tracer of sea salt and multiply its concentration with a factor to obtain an estimate of fresh sea-salt aerosol, including all the chloride. Hence, when one would keep both the sea-salt estimate and the full coarse mode nitrate in the chemical mass balance, the sea salt and nitrate contributions cannot simply be added as the nitrate replaces chloride. Consequently, one needs to make a correction in the chemical mass balance approach for this double counting.

In principle, there are two options to remove the double counting. The first is to remove the lost chloride mass from the sea salt estimate and to keep the coarse nitrate as it is. The second option is to assign only the net mass addition to the coarse nitrate part. The first option reflects the measured chemical composition of the particles. The second option reflects the sources and especially the associated reduction potential. Though both choices are valid and defendable, it can be argued that the second option suits better if we are after the source apportionment. Reduction of NO_x emissions may cause a reduction of coarse mode nitrate, which is partly compensated by the fact that chloride is not lost anymore. Such a reduction would yield a net result of $((NO_3\text{-}Cl)/NO_3 = (62–35)/62 =)$ 27/62 times the nitrate reduction (where the number involved are molar weights of the respective components). Hence, the same factor could be used to scale back the coarse nitrate fraction in the chemical mass balance. The motivation would be that when all anthropogenic sources would be non-existing one still has the sea salt left that is given now in the mass distributions. Doing so, the coarse nitrate would, on average, be lower with some 0.6 $\mu g\,m^{-3}$ which gives an increase in the NA part of the coarse fraction with some 4%. A similar reasoning may be valid for the anthropogenic sulphate in the coarse fraction. Corrections like these are uncommon in current mass closure studies and consequences will have to be explored in more detail in future.

4.4 Natural fraction

For policy makers the extent to which particulate matter can be influenced by measures is of importance. It is the anthropogenic part that could be targeted by abatement strategies. Here, a first-order approximation of the natural and anthropogenic contribution to PM_{10} and $PM_{2.5}$ is developed.

Sea spray emissions are the most important natural source of primary *sulphate*. Applying the sodium-to-sulphate ratio learns that roughly 5% of the particulate sulphate is marine. Though sulphate may be emitted directly into the atmosphere, its major source is the oxidation of sulfur dioxide. In the Netherlands anthropogenic SO_2 emissions derive mostly from the combustion of sulfur containing fuels for power generation and international shipping. In Europe, natural emissions for SO_2 include volcanoes but given location, height and distance to the Netherlands their contribution is probably low (i.e., not more than 1% to ground level sulphate). Contributions of other biogenic sources of SO_2 like oxidation of DMS, COS and H_2S are also of minor importance (Bates et al., 1992). Wildfire emissions of SO_2 are commonly neglected in studies directed to wild land fire emissions. In short, the natural contribution to sulphate in the Netherlands is estimated to be 5–10%.

To estimate how much of the *nitrate* is natural NO_x emissions from soil, biomass burning and lightning should be considered. Studies on NO emissions from soil report emissions between 59 and 190 kt in the EU15 (Simpson et al., 1999; Friedrich et al., 2008). Relative to the total inventoried emissions the central value is 4%. From these emissions about two third is attributed to agricultural soils and one third to forest soils. Soil NO_x emissions largely depend on the nutrient input (through fertilization or atmospheric deposition) implying that the abovementioned contribution is only partly natural. Lightning depends linearly on the amount of convective precipitation. In Europe corresponding emissions are estimated to be about 1% (65 kt) of the total inventoried emissions It mainly takes place between 1 and 5 km altitude and mostly in southern Europe (Meijer et al., 2001; Friedrich et al., 2008). The available wild fires estimates range between 20–50 kt (Friedrich et al., 2009; Hoelzemann et al., 2004) and also occur mostly in countries around the Mediterranean. Given the short life time of NO_x and the rather short transport distance of nitrate we assume the impact of lightning and wild land fires can be negligible (<1%) in the Netherlands. In short, the natural fraction of NO_x emissions and therewith nitrate is estimated to be 5% (absolute upper limit).

Ammonia is emitted from, most notably, animal manure, traffic and fertilizer application (Olivier et al., 1998). Emissions in Europe are for the largest part (80–95%) associated with agricultural activities (Van der Hoek, 1998). Recently, Erisman et al. (2009) estimated the natural emissions at about 10% of the total emission in Europe. This percentage includes contributions from wild animals and wetlands. A similar percentage is assumed for the Netherlands.

Elemental carbon is emitted from combustion processes and a pure primary component. The main source is the (incomplete) combustion of fossil fuels. Wild land fires are occasional sources of vast amounts of carbonaceous particles. Though wild land fires may seem natural, the vast majority of present day fires are due to human behavior. Hence, elemental carbon is almost exclusively anthropogenic.

Organic matter is released from combustion processes, agricultural activities, as well as from nature. Anthropogenic combustion particles (as well as small contribution of stable emissions) are inventoried. About half of the observed concentrations of OC (Schaap et al., 2004; Simpson et al., 2007) can be explained. Other primary sources include biological material (fungal spores and plant debris) may contribute up to 0.4 $\mu g\, m^{-3}$ (about 6% of OM) at rural background sites in central Europe (Sanchez-Ochoa et al., 2008). Recently, ^{14}C analysis suggested that some 70% (Ten Brink et al., 2010) of the OC mass in the Netherlands was of living material where agriculture and other landscaping activities may have contributed. The complicating factor in the estimation of the natural part of OM is the uncertainty related to its secondary component (oxidation of VOCs yields products with low vapor pressures that may condense on existing aerosol) as the major formation routes are not well known.

Similarly, the ratio of natural to anthropogenic SOA is under large scientific debate. Note that the oxidation pathways that yield SOA are largely influenced through hydroxyl and ozone from anthropogenic emissions. Presently, it is postulated that biogenic sources are a major contributor to atmospheric SOA (e.g., Simpson et al., 2007). Assuming that the unexplained OC using present day emission inventories is for the largest part SOA an upper limit of ~50% of natural OM is obtained. As a substantial part of the SOA may very well be anthropogenic we postulate a second guess with half of the SOA as natural, leading to 25% of natural OM.

Mineral dust originates from different sources, e.g., wind erosion of bare soils, agricultural land management, re-suspension of road dust, road wear, driving on unpaved roads, handling of materials and building and construction activities. The contributions of these sources are still poorly understood. Here, only wind erosion is relevant as natural source. Globally the atmospheric input through wind erosion is dominated by a few areas exceptionally susceptible for wind erosion. Saharan dust is regularly transported to countries around the Mediterranean Sea. In central and northern Europe dust transport from the Sahara occurs once or twice a year and is not considered very significant. During this study we could only identify one day with a significant impact of Saharan dust to PM (contribution ~4% of the annual mean MD concentration). Korcz et al. (2009) and Schaap et al. (2009) show that wind blown dust at the European continent is a much smaller source for dust than traffic re-suspension and agricultural land management. More importantly, the wind blown dust source strength from soils other than arable land is low. Hence, wind blown dust emissions are strongly related to anthropogenic changes in surface vegetation cover and are regarded as mostly anthropogenic. Consequently, the total mineral dust concentration in air is expected to be anthropogenic for a large part. To be on safe side an upper limit of 20% of the mineral dust is assumed to be of natural origin.

Metals originate from a vast range of abrasion processes and metallurgy industry. Though soils may contribute to metal concentrations they are in principle accounted for in the mineral dust estimate. Here, all metals are assumed to be anthropogenic.

The natural fraction of the *unknown mass* is by definition unknown. As water partly explains the unknown fraction and most of the water appears associated with SIA it is likely that a significant part of the unknown fraction can be considered to anthropogenic. We assume here that the anthropogenic/natural ratio within the unknown mass fraction resembles that of the explained mass.

The natural fraction in the Netherlands is then obtained by adding relative natural mass contributions per component. For instance, in Hellendoorn 11.5% of PM_{10} is associated with sea salt adding to 11.5% of natural PM_{10} (see Table 5). Nitrate contributes 21 % of which 5% is assumed to be natural resulting in a contribution of 1% natural PM_{10}. Adding all contributions, the estimated natural fraction of PM_{10} is 25%. The low estimate for carbonaceous particles yields a natural fraction of 21%. Hence, around one quarter of PM_{10} is estimated to be natural. Performing the same exercise for $PM_{2.5}$ yields estimates of 18 and 14% for the two cases, respectively. Application of this methodology to all sites in this campaign yields natural fractions of about one fourth for PM_{10} and one fifth for $PM_{2.5}$ (Fig. 6). In case of the low natural OM fraction the natural estimates are about 5% lower than with the high case.

5 Conclusions

There is a considerable conformity in the chemical composition of PM over the Netherlands. Most dominant is the secondary inorganic aerosol – the sum of sulphate, nitrate and ammonium – showing slightly higher levels at the rural sites. Carbon containing components are generally the second largest contributor being enhanced in the traffic dominated urban area. The most important natural constituent is sea salt, especially in the western part of the Netherlands near the North Sea. Contributions of mineral dust and metals appear relatively low. The distribution of species in PM_{10} resembles that of $PM_{2.5}$ which is not surprising as the mass of $PM_{2.5}$ is about two thirds of the total PM_{10} mass. The chemical composition observed in the coarse mass fraction appears more balanced: contributions of mineral dust and sea salt are of comparable magnitude with those of SIA and TCM.

On days with high PM concentrations, all constituents, except sea salt, show higher concentrations. Sea salt maximises in marine air masses associated with clean air conditions. The nitrate and unknown contributions increase most on these days suggesting a relationship by means of the associated water content. The relative contribution of the remaining components is mostly stable as function of PM concentration.

After analysing the filter samples on chemical content the sum of all the components accounts on average for 70–80% of the total mass. Hence, a full analysis is not obtained, but existing knowledge can be used to narrow down partially the remaining gap. For example, metals can be taken into account as their oxides and total carbonaceous matter (including non-C atoms) is estimated based on the total carbon content. In addition, the contributions of mineral dust and sea salt were estimated. After this procedure, 80–94% of the total mass can be explained. Uncertainties occurring in the mass closure are conversion factors for total carbonaceous matter and the displacement of chloride by nitrate in the coarse fraction.

Based on a literature review, it is concluded that the most important natural contributions originate from sea salt (100%) and organic material (with an upper limit of 50%). Including the natural parts of the remaining constituents, estimates for the entire natural contribution yield 25% for PM_{10} and 20% for $PM_{2.5}$. This (fairly pragmatic) analysis illustrates that the majority of PM in the Netherlands is of anthropogenic origin.

A major gap in knowledge remains the characterisation of the unknown mass and the role of the water content of the filter. Another caveat is the chemical characterisation of the urban increment between (with respect to rural background concentrations). The technical inability in the differentiation between EC and OC influences results. For more traditional PM components, like SIA and primary material, a modelling may identify source contributions at sector level, and provide insight into national versus foreign sources. The origin of carbonaceous matter remains one of the biggest challenges, as knowledge in this respect is still moderate.

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Table 1. Properties of the measurement locations.

Location	Characteristics
Cabauw	Background location in the centre of the Netherlands Rural surrounding Some agricultural emissions in the direct surroundings Urban areas in 20–40 km distance
Hellendoorn	Background location in the east of the Netherlands Rural surrounding No known anthropogenic emissions nearby
Vredepeel	Background location in the southeast of the Netherlands Rural surrounding Intensive live stock (pigs) breeding nearby
Schiedam	Urban background location in the west of the Netherlands Part of Rotterdam urban agglomeration (appr. 600 000 inhabitants) Residential areas surrounded by motorways Close (<5 km) to industrial activity (refineries, oil-industry) and harbour
Rotterdam	Traffic location ("kerbside") in the west of the Netherlands Part of the Rotterdam agglomeration Less than 5 m from the kerb; traffic junction at 80 m Heavy traffic

Table 2. Average concentrations of the main components as measured at the five sites.

	Hellendoorn	Vredepeel	Cabauw	Schiedam	Rotterdam
number of samples	38	35	26	33	41
PM_{10}	17.7±6.4	21.2±7.3	23.6±11.9	21.8±9.6	26.3±11.6
NO_3	3.6±2.1	4.3±2.2	5.4±3.7	4.0±3.6	4.8±4.2
SO_4	2.3±1.0	2.5±1.1	3.0±1.4	3.1±1.6	3.0±1.6
NH_4	1.2±0.7	1.5±1.1	2.0±1.7	1.2±1.6	1.5±1.7
EC	1.7±1.0	2.0±0.9	2.1±1.0	2.0±1.3	3.7±1.5
OC	1.6±1.0	1.8±0.7	1.6±0.9	1.8±1.3	2.3±1.0
Cl	0.6±0.9	1.1±1.2	0.4±0.4	1.2±1.3	0.9±0.9
Na	0.6±0.6	0.9±0.8	0.5±0.4	1.1±0.8	0.9±0.6
total metals	1.4±0.8	1.7±0.7	2.0±1.2	2.0±1.0	2.9±1.1
not-analysed	4.6±3.5	5.5±2.5	6.7±4.5	5.3±2.5	6.4±3.3
$PM_{2.5}$	12.5±5.4	14.5±6.3	17.5±11.0	13.0±7.6	16.4±10.0
NO_3	2.6±1.7	3.2±2.3	4.1±3.7	2.5±2.5	3.0±3.0
SO_4	2.1±0.9	2.2±1.1	2.7±1.4	2.5±1.3	2.4±1.1
NH_4	1.3±0.9	1.3±1.0	1.6±1.4	1.1±1.2	1.4±1.5
EC	1.5±0.8	1.4±0.7	1.7±0.9	1.9±1.0	3.2±1.4
OC	1.4±0.7	1.2±0.6	1.3±0.6	1.2±0.7	1.5±0.8
Cl	0.2±0.2	0.3±0.4	0.2±0.1	0.2±0.2	0.2±0.2
Na	0.2±0.2	0.3±0.3	0.1±0.1	0.3±0.2	0.3±0.3
total metals	0.7±0.4	0.7±0.2	0.8±0.3	0.9±0.3	1.0±0.3
not-analysed	2.6±2.0	3.8±2.7	4.9±5.7	2.4±2.3	3.3±3.6
$PM_{10-2.5}$	5.1±2.1	6.8±2.9	6.1±2.5	8.8±3.6	9.9±3.4
NO_3	1.0±0.9	1.1±1.0	1.3±2.7	1.5±1.6	1.8±1.7
SO_4	0.2±0.4	0.3±0.5	0.2±1.1	0.6±0.8	0.6±1.0
NH_4	−0.1±0.6	0.2±0.4	0.4±1.0	0.1±0.6	0.1±0.5
EC	0.2±0.9	0.6±0.7	0.4±0.3	0.2±0.9	0.4±0.6
OC	0.2±0.8	0.7±0.6	0.3±0.4	0.5±1.0	0.8±0.6
Cl	0.4±0.7	0.7±0.9	0.3±0.3	1.0±1.2	0.7±0.7
Na	0.4±0.5	0.6±0.5	0.4±0.3	0.8±0.6	0.6±0.5
total metals	0.7±0.6	0.9±0.5	1.2±0.9	1.2±0.8	1.9±0.9
not-analysed	2.1±2.6	1.6±2.5	1.7±5.0	2.9±1.6	3.0±2.3

Table 3. Absolute and percentual change in mass concentration after applying converson formula.

	PM_{10}		$PM_{2.5}$		$PM_{10-2.5}$	
	rural	urban	rural	urban	rural	urban
associated oxygen						
increase ($\mu g\,m^{-3}$)	0.9	1.2	0.3	0.4	0.5	0.8
%-decrease of "NA"	4%	5%	2%	3%	9%	8%
sea salt						
increase ($\mu g\,m^{-3}$)	0.8	1.3	0.3	0.4	0.6	0.8
%-decrease of "NA"	4%	5%	2%	3%	10%	9%
nss sulphate						
increase ($\mu g\,m^{-3}$)	–0.2	–0.3	–0.1	–0.1	–0.1	–0.2
%-decrease of "NA"	–1%	–1%	0%	0%	–2%	–2%
total carb. material						
increase ($\mu g\,m^{-3}$)	1.1	1.5	0.9	1.2	0.3	0.3
%-decrease of "NA"	5%	6%	6%	8%	4%	3%

Table 4. Concentrations of the constituents as determined in the PM_{10} and $PM_{2.5}$ data set for the five BOP-locations.

	Hellendoorn	Vredepeel	Cabauw	Schiedam	Rotterdam
number of samples	38	35	26	33	41
PM_{10}	17.7±6.4	21.2±7.3	23.6±11.9	21.8±9.6	26.3±11.6
SIA	7.0±3.4	8.0±4.2	10.2±6.4	8.0±6.6	9.1±7.3
TCM	4.3±2.4	5.0±2.0	45.0±2.3	4.9±2.5	7.7±3.1
SS	2.0±2.0	3.0±2.5	1.6±1.2	3.7±2.7	2.9±2.1
MD	1.2±1.4	1.2±1.0	2.1±1.9	1.6±1.3	1.8±1.3
metals	0.8±0.3	1.2±0.4	1.0±0.4	1.4±0.5	2.4±0.8
unknown	2.3±3.5	2.7±2.0	3.7±4.2	2.1±2.7	2.3±2.8
$PM_{2.5}$	12.5±5.4	14.5±6.3	17.5±11.0	13.0±7.6	16.4±10.0
SIA	6.0±2.8	6.6±4.1	8.4±6.1	6.0±4.6	6.8±5.1
TCM	3.8±1.9	3.3±1.5	3.9±2.0	4.0±2.2	6.1±2.7
SS	0.6±0.8	1.0±0.9	0.5±0.3	1.0±0.8	0.9±1.0
MD	0.5±0.4	0.5±0.3	0.7±0.4	0.6±0.5	0.6±0.3
metals	0.4±0.2	0.6±0.1	0.5±0.2	0.6±0.2	0.8±0.3
unknown	1.2±1.7	2.5±2.6	3.5±5.5	0.7±2.2	1.2±3.5
$PM_{10-2.5}$	5.1±2.1	6.8±2.9	6.1±2.5	8.8±3.6	9.9±3.4
SIA	1.0±1.5	1.4±1.6	1.8±4.5	2.0±2.8	2.3±2.9
TCM	0.5±2.0	1.7±1.4	1.1±0.9	0.9±0.9	1.6±1.1
SS	1.4±1.5	2.0±1.7	1.2±0.9	2.7±2.0	2.0±1.5
MD	0.7±1.0	0.8±0.7	1.4±1.5	1.0±1.2	1.2±1.0
metals	0.4±0.2	0.6±0.3	0.5±0.3	0.8±0.4	1.6±0.7
unknown	1.1±3.0	0.2±2.2	0.2±5.0	1.4±2.0	1.1±2.3

Table 5. Illustration of natural contribution (in %) for all components in the case of Hellendoorn. For each component the relative contribution to $PM_{2.5}$ and PM_{10} is listed as well as the estimated natural contribution. The two columns on the right provide the resulting natural contribution to PM_{10} and $PM_{2.5}$ for each component for a high and low estimate of the natural OC content. All numbers are percentages.

Comp	PM_{10}	$PM_{2.5}$	Natural	Hellendoorn	
	Contrib.			Low/high	
				PM_{10}	$PM_{2.5}$
NO_3	21	21	5	1	1
SO_4	13	17	5	1	1
NH_4	7	10	10	0.5	1
MD	7	4	20	1.5	1
SS	11.5	5	100	11.5	5
Metals	5	4	0	0	0
$EC^{*}1.3$	12	15	0	0	0
$OC^{*}1.3$	12	14	25/50	3/6	3.5/7
Sum known				18/22	12.5/16
Unknown	13	10	[1]	2.5/3	1.5/1.5
Total				21/25	14/18

[1] Natural contribution is assumed to be the same as the total natural percentage of the explained mass.

Fig. 1. Localisation of the five BOP measurement sites in the Netherlands.

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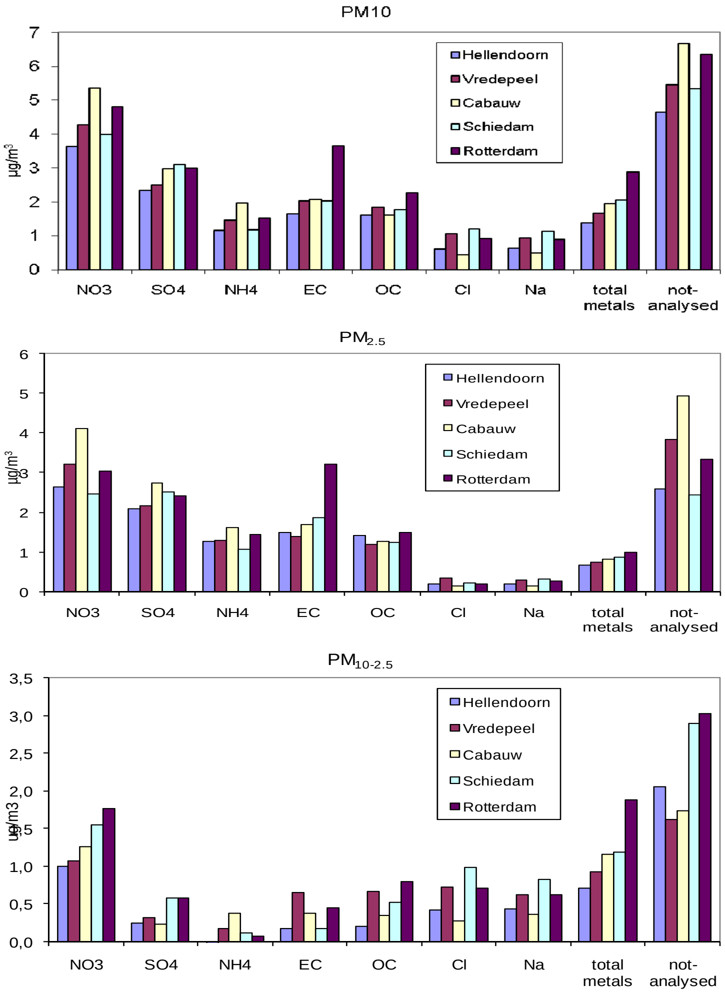

Fig. 2. Absolute concentrations at the five sites.

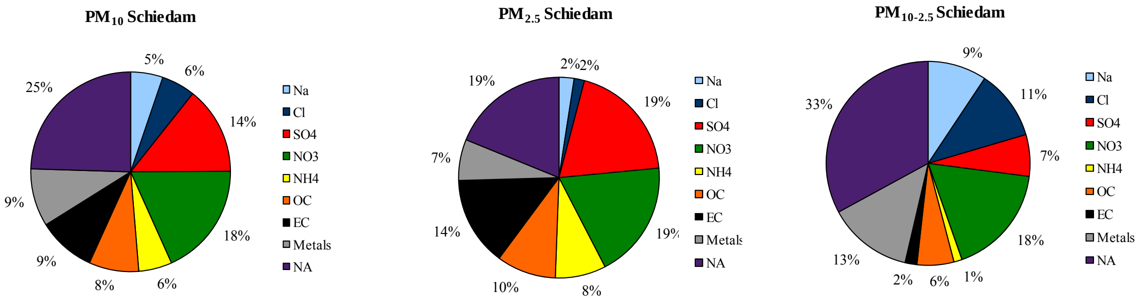

Fig. 3. Chemical distributions measured at the urban background site Schiedam.

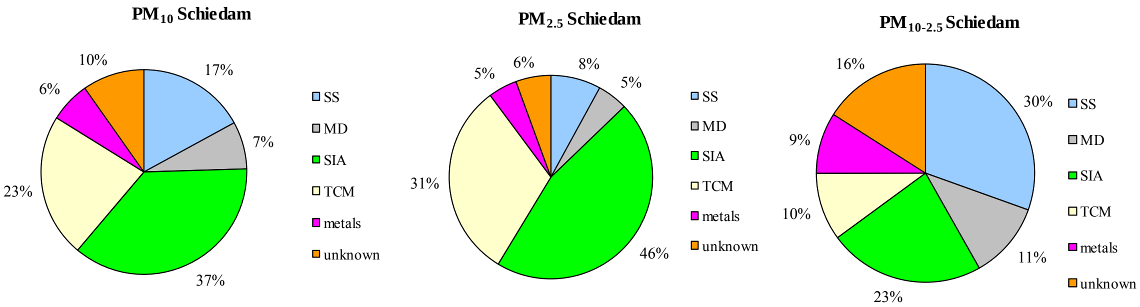

Fig. 4. Mass closures for the different fractions estimated at the urban background site Schiedam.

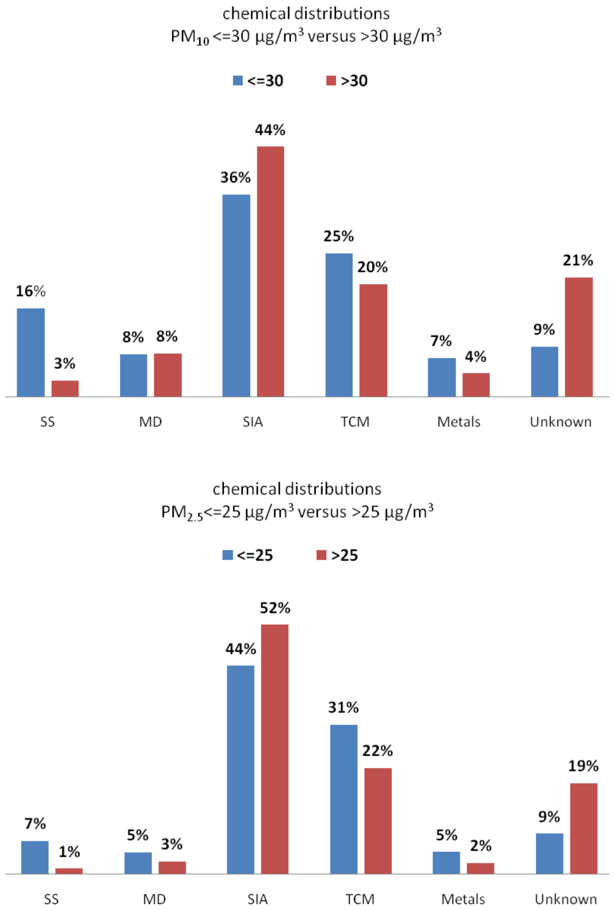

Fig. 5. Average chemical distributions in data subsets with high and low PM concentrations. Above: $\mathrm{PM}_{10} > 30\,\mu\mathrm{g\,m}^{-3}$ versus $\mathrm{PM} \leq 30\,\mu\mathrm{g\,m}^{-3}$; below $\mathrm{PM}_{2.5} \leq 25\,\mu\mathrm{g\,m}^{-3}$ versus $\mathrm{PM}_{2.5} > 25\,\mu\mathrm{g\,m}^{-3}$. Averages over the five BOP stations.

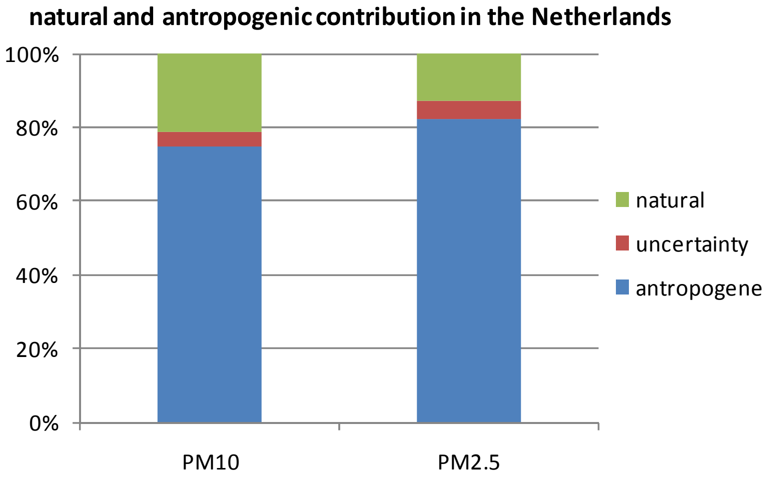

Fig. 6. Natural and anthropogenic contributions to PM_{10} and $PM_{2.5}$ as estimated from the BOP data set.