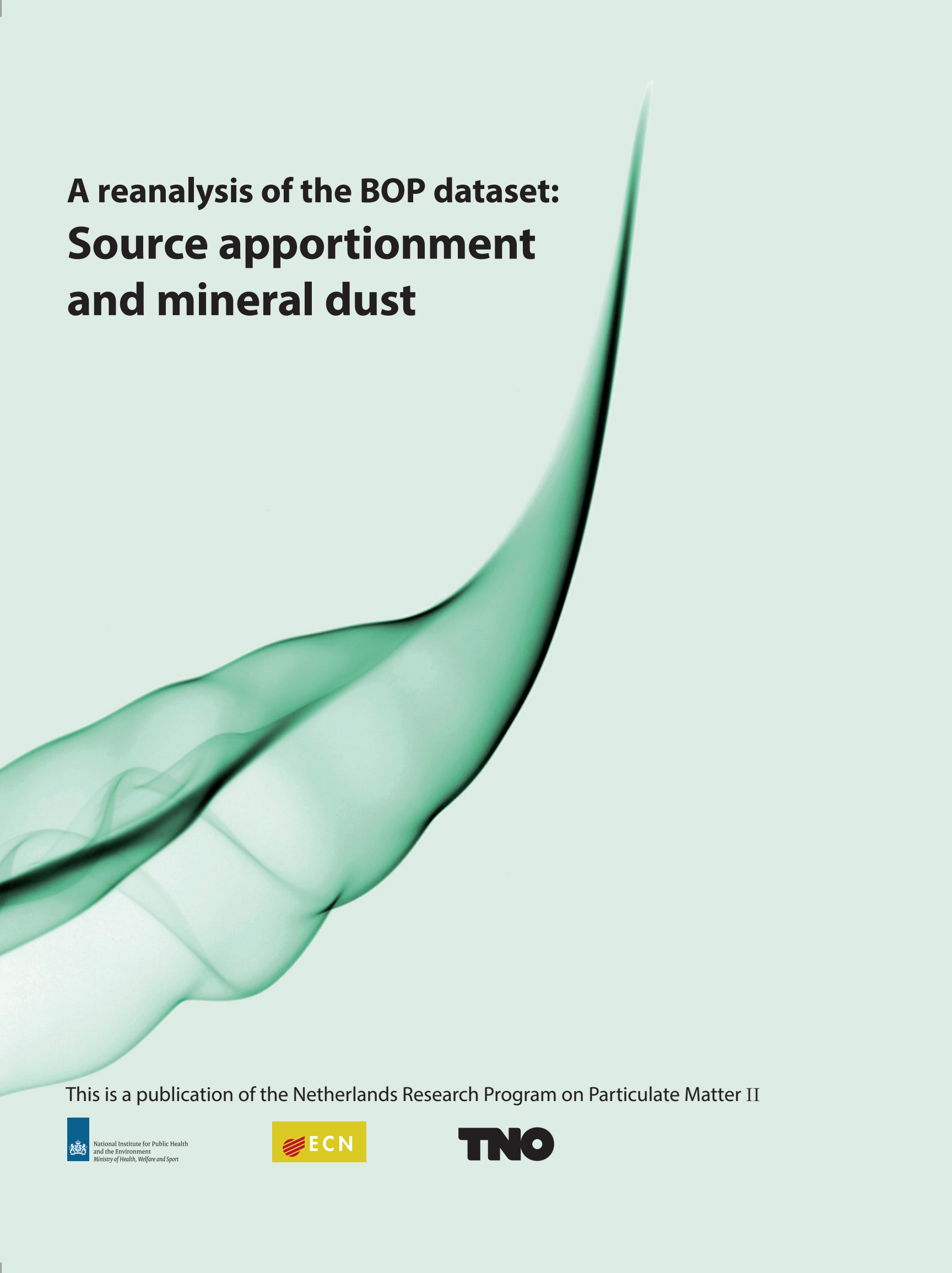




A reanalysis of the BOP dataset: Source apportionment and mineral dust

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National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport





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Abstract

A reanalysis of the BOP dataset

In order to determine the effect of policy measures on particulate matter concentrations, it is necessary to get accurate knowledge on the behavior of particulate matter. This report describes results from *scientific research* based on measurements and calculations of particulate matter. RIVM, TNO and ECN have performed detailed measurements on particulate matter at six locations in the Netherlands. These measurements were performed as part of the first Netherlands Research Program on Particulate Matter (BOP), which aimed at obtaining knowledge on the composition and distribution of particulate matter. The measurements made a distinction between the total amount of particulate matter (PM_{10}) and its finer fraction ($PM_{2.5}$). This BOP dataset also contains information on the chemical composition of PM. This composition provides important information about the sources of particulate matter, such as industry and traffic. However, some questions about the origin of particulate matter remained unanswered after the first BOP program. Because this lack of knowledge affects the understanding of the effectiveness of policy measures, RIVM has performed a reanalysis of the BOP dataset in the second BOP program, which focused on two questions.

Explanation for inconsistent composition of PM_{10} and $PM_{2.5}$ per source

Using a source apportionment technique (Positive Matrix Factorization), the PM_{10} and $PM_{2.5}$ datasets from BOP, were separately analyzed. The obtained results were similar for the main components of particulate matter. However, for elemental carbon (soot), the result was inconsistent. This inconsistency could result from the fact that the analysis was performed on each dataset separately. To check this, the analysis was repeated, this time on the combined dataset of PM_{10} and $PM_{2.5}$. The inconsistency was however not resolved. This means that the source of soot, using the source apportionment analysis, is still not fully understood. Further analysis of the existing data set will probably not answer this question. The fact that the result is not changed by the different PMF, means that the analysis, which is also promoted by the EU, is more robust than expected.

Differences between mineral dust contribution to PM in the Netherlands and Flanders

The second question concerned the contribution of mineral dust to PM_{10} concentrations. According to previous calculations, mineral dust concentrations in Flanders were twice as large as compared to concentrations in the Netherlands. Here it is shown that this difference can largely be explained by the used calculation method. It is shown that in the Flemish calculation some chemical components are assessed differently than in the Netherlands, hence the difference. Therefore, in this case the differences are not attributable to the measurement data. Hence, the results are therefore sufficient for reliable estimates of source contributions and the possible effect of policy measures.

Keywords: particulate matter, mineral dust, positive matrix factorization

Rapport in het kort

Een heranalyse van de BOP dataset

Om het effect van beleidsmaatregelen te kunnen inschatten is kennis van het gedrag van fijn stof essentieel. Dit rapport beschrijft een wetenschappelijk deelonderzoek van metingen en berekeningen van fijn stof. RIVM, ECN en TNO hebben op zes locaties uitgebreide metingen uitgevoerd van de concentraties fijn stof (PM) in de lucht. De metingen zijn uitgevoerd voor het eerste Beleidsgericht Onderzoeksprogramma PM (BOP), dat erop gericht is om kennis te verwerven over samenstelling en verspreiding van fijn stof. Bij de metingen is onderscheid gemaakt tussen de totale hoeveelheid fijn stof (PM₁₀) en de fijnere fractie ervan (PM_{2,5}). De dataset bevat informatie over de chemische componenten waaruit fijn stof is opgebouwd. Deze samenstelling geeft belangrijke informatie over de bronnen van fijn stof, zoals industrie en verkeer. Enkele vragen over de herkomst van fijn stof bleven na het eerste onderzoek onbeantwoord. Omdat dit invloed heeft op het inzicht in de effectiviteit van maatregelen, heeft het RIVM twee van deze vragen in het kader van het tweede BOP-programma nader onderzocht via een beperkte heranalyse van de data.

Verklaring voor inconsistente samenstelling PM₁₀ en PM_{2,5} per bron

Via een geavanceerde bronanalyse techniek (Positive Matrix Factorisation) zijn de PM₁₀ en PM_{2.5} datasets in BOP apart geanalyseerd. De resultaten waren voor de belangrijkste componenten goed vergelijkbaar. Voor één component, elementair koolstof (roet), was het resultaat inconsistent. Die inconsistentie zou kunnen komen doordat de analyse op de beide datasets afzonderlijk is uitgevoerd. Om dit te controleren is de analyse herhaald op de gecombineerde dataset. De inconsistentie was daarmee niet verdwenen. Dit betekent dat de herkomst van roet nog steeds niet geheel bekend is. Verdere analyses van de bestaande data set zullen vermoedelijk deze vraag niet beantwoorden. Het feit dat het resultaat niet veranderd door de PMF analyse anders uit te voeren betekent dat een dergelijke bronanalyse, die ook door de EU wordt gepropageerd, robuuster is dan verwacht.

Verschillen tussen Nederland en Vlaanderen in bijdrage bodemstof

De tweede vraag betrof het aandeel dat opwaaiend bodemstof levert aan de concentratie van PM₁₀ in de lucht. Volgens eerdere berekeningen zou bodemstof in Nederland de helft minder bijdragen aan de fijnstofconcentratie dan in Vlaanderen. Dit verschil blijkt grotendeels verklaard te kunnen worden door de gebruikte definitie van bodemstof. In Vlaanderen bevat de definitie van bodemstof meer componenten. Met dezelfde definitie blijken de resultaten goed vergelijkbaar. De resultaten zijn daarom voldoende betrouwbaar voor schattingen van bronbijdrage en het mogelijke effect van maatregelen.

Trefwoorden: fijn stof, bodemstof, positive matrix factorization

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Summary

The Netherlands is one of the hotspot areas in Europe with high concentrations of particulate matter (PM). On the initiative of the former ministry of VROM detailed measurements of the concentrations of particulate matter (PM) in the air have been performed from August 2007 to September 2008 at six locations in the Netherlands. The measurements were carried out in the context of the first edition of the Policy Oriented Research Program PM (BOP), which aims to acquire knowledge about particulate matter. A distinction during the measurements was made resulting in measurements for both the total amount of particulate matter (PM_{10}) and its finer fraction ($PM_{2.5}$). Besides total mass the chemical composition has been established for each fraction resulting in a dataset which includes information on the chemical components of particulate matter.

The source apportionment technique *Positive Matrix Factorization (EPA-PMF)* was applied to the dataset in the first BOP programme (Schaap et al., 2010). This was done in order to identify and quantify the most relevant source contributions of PM and their spatial variability in the Netherlands. Separate EPA-PMF calculations were performed for the $PM_{2.5}$ and PM_{10} datasets. The results of the EPA-PMF calculations showed a number of strong similarities between the two PM sets, both for composition and contributions. These similarities are due to the chemical resemblance of both PM sets.

The source apportionment study of the BOP dataset also gave some differences in the composition of PM_{10} and $PM_{2.5}$ originating from the same source factor. Elemental carbon (EC) showed the strongest difference, the mass was distributed across different source factors in both fractions. In this report we try to explain this behavior by means of a new calculation with EPA-PMF, combining the $PM_{2.5}$ and PM_{10} dataset. The results of this calculation showed six unique source types for the combined PM dataset, quite similar to the results of the separate analysis of each PM fraction. This indicates that the EPA-PMF method, used in the analysis of the BOP programmes, is a very robust method.

This research also shows that most of the EC mass is still contributed to a different source factor for $PM_{2.5}$ than for PM_{10} . Since the EPA-PMF method was shown to be very robust, this implies that the difference is implicitly present in the dataset. The cause of the inconsistencies in the dataset remains unclear, although a number of options have been excluded.

In addition, a re-analysis of the contribution of mineral dust to PM in the Netherlands is performed. The results from BOP showed that the mineral dust concentrations were on the low end as compared to nearby countries abroad (Flanders & Germany) and earlier estimates for the Netherlands as made by Visser et al., (2001).

Our study shows that the difference in mineral dust contribution in PM as measured in the Netherlands and Flanders is mainly caused by the difference in definitions (equations) of mineral dust.

1 Introduction

High concentrations of particulate matter (PM) correlate with negative health effects. Particulate matter consists of contributions from many different substances originating from a variety of sources. Epidemiological studies have shown both long-term and short-term exposure to PM leads to major health effects in humans. The health effects of PM exposure to humans are dependent of the composition of the PM. Because PM itself is a 'container-term' of different type of particles, knowing the composition of PM is of importance in order to allow for distinction between different components and sources of PM. Development of mitigation strategies for PM is therefore both an important and difficult task.

In the framework of the first Netherlands Research Program on Particulate Matter (BOP I), an intensive one-year measurement campaign from August 2007 to August 2008 was carried out. During this period $PM_{2.5}$ and PM_{10} were sampled simultaneously every other day at several locations: Vredepeel, Cabauw and Hellendoorn (rural background stations), Schiedam (urban background) and Rotterdam (traffic station) and additionally for PM_{10} on Breda (traffic station). Approximately half of the sampled filters were chemically analysed on its composition. In this way the BOP dataset gave a very detailed overview of the composition of both $PM_{2.5}$ and PM_{10} in the Netherlands (Schaap et al., 2010). The major components of PM in the Netherlands were found to be secondary inorganic aerosols, total carbonaceous matter, mineral dust, sea salt and heavy metals. The information of the chemical composition of PM at the locations allows one to trace the PM sources, using a statistical analysis called positive matrix factorization (PMF). This method also allows one to contribute specific mass fractions of PM to the several sources found.

Detailed information on sources can be used as input for physical-chemical deterministic models like the LOTOS-EUROS model, the EMEP model or OPS. Although the progress in these deterministic models is impressive, all models continue to severely underestimate the measured levels of PM. The source contributions as found by PMF can be used to identify and clarify areas where an underestimation occurs (Schaap et al., 2010).

In the first evaluation, BOP I (Schaap et al., 2010), both the $PM_{2.5}$ and PM_{10} data sets were separately analysed using PMF. By using separate analyses there are no mathematical incentives to produce comparable solutions between both sets. Even so, the solutions, presumably due to the chemical resemblance, show a number of strong similarities, both for composition and contributions. For both $PM_{2.5}$ and PM_{10} the major sources identified in BOP I with this PMF analysis were: 1) nitrate-rich secondary aerosol, 2) sulphate-rich secondary aerosol, 3) traffic and resuspended road dust, 4) metal from industrial activity/incineration, 5) sea salt, 6) mineral dust, and 7) particles from residual oil combustion.

However, some features are different in the $PM_{2.5}$ and PM_{10} factors. Parts of these differences are possibly explained by the fact that using PMF does not ensure a unique solution. In theory there might be other (different) solutions which fulfill the model constraints as well. This effect, called rotational freedom, might be responsible for the differences between the $PM_{2.5}$ and PM_{10} solutions.

In an attempt to clarify the origin of these differences, a combined analysis of both PM fractions is performed. Similar work has been performed by Karanasiou et al. (2009). While the average contribution of the PM_{2.5} and PM₁₀ data is obviously different, both PM_{2.5} and PM₁₀ have to follow the same pattern in time and space. This assumption can be checked by using PMF on the combined data set. In case PM_{2.5} and PM₁₀ composition appear to be very different from each other, a split of a single factor found in BOP I in two separate factors is expected. Furthermore, combining the sets will also limit the rotational freedom. Hence, if the same different features are observed these are probably not related to the rotational freedom in PMF.

Finally, a re-analysis of the contribution of mineral dust to PM in the Netherlands is performed. The results from BOP showed that the mineral dust concentrations were on the low end as compared to nearby countries abroad (Flanders & Germany) and earlier estimates for the Netherlands as made by Visser et al. (2001).

The PMF analysis is discussed in sections 2, 3 and 4 of this report, the re-analysis of mineral dust is discussed in section 5 of this report. Finally, in section 6 we summarize the results.

2 PMF analysis

2.1 Introduction

During our first study of the BOP dataset we have applied EPA-PMF to both the $PM_{2.5}$ and PM_{10} measurements separately. These results are described in more detail by Schaap et al. (2010) and in Mooibroek et al. (2011). In this previous study we combined the data from all sample sites, five sites for $PM_{2.5}$ and six sites for PM_{10} , to generate both a $PM_{2.5}$ and a PM_{10} data set. After pre-processing the data we applied positive matrix factorization (PMF) using the widely available EPA-PMF programme and evaluated the results separately.

Comparing the results from both data sets proved to be a difficult task. Not only another sample site was added to PM_{10} , but there were also differences in sample days in each set due to the separate pre-processing. We made a general comparison of the found source profiles for both data sets and found a good agreement between the $PM_{2.5}$ and PM_{10} source profiles. However, some anomalies were also detected. One of these anomalies was the difference in apportionment of elemental carbon (EC) between the $PM_{2.5}$ and PM_{10} source profiles. In $PM_{2.5}$ the majority of EC was apportioned to a factor related to traffic emissions with the addition of resuspended road dust. However, in PM_{10} the majority of EC was found in the factor classified as 'sulphate-rich secondary aerosol'. At that point we were unable to provide an explanation for this behaviour.

In an attempt to make the comparison between both $PM_{2.5}$ and PM_{10} more easily and explain the strange anomalies found in the separate analysis in this study, we have combined not only the sample sites, but also both mass fractions.

For more information about the methodology and underlying mathematics of EPA-PMF see also Appendix A.1.

2.2 Combining the datasets

The starting data sets for both $PM_{2.5}$ and PM_{10} are the sets that have been used in the separate analysis (Schaap et al., 2010; Mooibroek et al., 2011). The data has undergone a pre-processing process keeping only those sample days with complete ICP-MS measurement results; sample days without ICP-MS have been omitted. The ICP-MS analysis is responsible for measuring most of the species, 28 species of a total of 34 species (excluding total mass) and contains several tracer species which can be used to identify sources. Furthermore, as described in Schaap et al. (2010) and Mooibroek et al. (2011) we used both validated and rejected data; rejected data are weighted in the EPA-PMF analysis correspondingly based upon the validation codes using the uncertainty matrix.

Using these separate data sets as a starting point ensures that the combined data set is primarily filled with data from both $PM_{2.5}$ and PM_{10} with complete ICP-MS measurement results for either one or both of the mass fractions.

We combined the data sets on each sample site based upon sample date using all possible sample dates from 1 August 2007 – 1 October 2008. For each unique combination of sample site and sample date we looked for the measured concentration for both the $PM_{2.5}$ and PM_{10} dataset. However, since the measurements were not performed daily the majority of the new sample days

do not have any data associated with it. We created a new set by removing these days from the set. This set contains only sample days for which either ICP-MS measurement for $PM_{2.5}$ or PM_{10} or both are available. Descriptive analyses of the ICP-MS measurement results of the combined set for each sample site are given in Table 1.

Table 1 Descriptive analysis of the combined $PM_{2.5}$ and PM_{10} data set (ICP-MS measurements only)

Sample site	$PM_{2.5}$ + PM_{10}	Only $PM_{2.5}$	Only PM_{10}
Schiedam	83	4	4
Vredepeel	108	5	6
Rotterdam	111	4	8
Cabauw	78	4	5
Hellendoorn	69	13	10
Total	449	30	33

In Table 1 it can be seen that the majority of the sample days for each sample site contains both $PM_{2.5}$ and PM_{10} results. There are, however, some sample days that either contain only $PM_{2.5}$ or PM_{10} results.

Besides the species measured by the ICP-MS method there are also some other species measured by other analysis methods. These species are Elemental and Organic Carbon (Keuken and Ten Brink, 2010?; Schaap et al., 2010), ammonium, sulphate and nitrate aerosol and chloride (Weijers et al, 2010; Schaap et al., 2010).

During the BOP campaign the measurements of EC, OC, secondary inorganic aerosol (SIA) and chloride were not quite in sync with the ICP-MS measurements. This behaviour leaves us with missing data, e.g. gaps for several sample days.

Since positive matrix factorization (PMF) is designed to deal with a 'complete-case' data set (for all samples data are available for all measured parameters) we would like to minimize the amount of missing data. Data that are missing should be filled by artificial values and weighted accordingly before use in PMF. However, even with weighting applied there is always chance the chosen approach influences the final solution found by PMF. By minimizing the amount of missing data the likelihood of this influence is decreased.

We found that sample days with either $PM_{2.5}$ or PM_{10} ICP-MS results were also missing the information from EC/OC/SIA/Cl measurement. We have decided to omit these sample days from the final data set used in PMF.

In line with the previous study this leaves us with combined data set where ICP-MS results in both mass fractions are available. This leaves a set of 449 sample days, with no missing values for ICP-MS measured species and approximately 149 sample days (33%) missing for $PM_{2.5}$ and 150 sample days (33%) missing for PM_{10} EC/OC/SIA/Cl measurements for all five sample sites.

2.2.1

Combining locations

The data set consists of five different sample sites, each containing approximately 80 – 115 measurements made during the period of September 2007 – August 2008. Earlier work (Bloemen et al., 2008; Schaap et al., 2010; Mooibroek et al. 2011) used the assumption there is not much

variance between the elemental compositions of the sources on each site, most variance is suspected to be found in the contribution of each individual source on each location. For example, in a relative small country like The Netherlands, a contribution from the traffic factor is expected at all sites. However, this contribution has to be predominately higher at a traffic related receptor site compared to a rural receptor site.

Combining the data set will provide insight in sources affecting all five receptor sites, and will most likely tend to focus on the global sources instead of the local contributions.

Based upon this assumption we have combined data from all sites into one data set prior to applying PMF. Subsequently, after the analysis the source contributions have been split up to the original five sites.

Since measurements on all sites were conducted in the same period, combining the dataset proved to be a challenge. It was decided to change the year of the measurement date so all sites would be measured in a different year. This approach will cause a problem when looking at the contribution of for example weekdays and weekends. Therefore we have shifted the dates slightly to keep the information for weekdays and weekends intact.

2.3 Dealing with missing data

We used multiple imputation (MI), first proposed by Rubin (1976, 1977) and frequently applied in the fields of environmental research and biostatistics (Hopke et al., 2001; Baccarelli et al., 2005; Ibrahim et al., 2005; Yang et al., 2005) to fill in the missing data.

After the imputation we compared the species correlations between $PM_{2.5}$ and PM_{10} found in measured data with the data including imputed values. If there is a huge influence of the imputed values changes in correlations are expected. For EC/OC/SIA/CI changes in correlations between $PM_{2.5}$ and PM_{10} were indeed detected, the largest change was found for OC. The concentrations of organic carbon show a high degree of randomness between the $PM_{2.5}$ and PM_{10} fractions with the imputed values lying within the boundaries.

Based upon this check we conclude that the imputed values follow the pattern found in the measurements. Hence we feel that the influence of the imputed values is likely to be limited if appropriate weighing is used in the PMF analysis.

More detailed information about the procedure used to deal with missing values and the subsequent correlation analysis can be found in Appendix B.

2.4 Using samples with indicative mass

Several quality assurance tests were performed on the measurements to ensure the validity of the results. Most of the quality assurance tests focused on the total mass measurements. For example, strict rules were used for the setting of the temperature and relative humidity of the weighing room. If the total mass measurement failed these strict criteria all subsequent analyses (ICP-MS, EC/OC/SIA/CI) were rejected. However, in most cases the rejected samples still contain useful information, albeit with a higher uncertainty.

Positive matrix factorization (EPA-PMF) uses the uncertainty matrix to apply weights for each separate measurement. This allows us to include certain

samples which might not meet the initial strict requirements, but might still contain useful information.

We have included these samples in our analysis and weighted the corresponding results accordingly, based upon the underlying reason leading to the initial rejection.

2.5 Selecting species in factor analysis

Not every chemical species in the speciated sample matrix X may provide valuable information to solve the PMF problem. In fact, Paatero and Hopke (2003) found including all species in factor analytical models may actually degrade the solution. In this study Paatero and Hopke suggest using the signal-to-noise ratio (S/N) for each species as an indicator to qualify species either as strong enough to be included in the model; bad enough to be severely down-weighted, if not removed; or weak (between strong and bad), but retainable in the model and slightly down-weighted.

Primarily based upon the S/N ratio and guided by the percentage of samples below the detection limit, the classification for each species was established. Detailed information about the $PM_{2.5}$ species and classification are given in the tables in Appendix A.

Species categorized as weak were retained in the analysis whereas species categorized as bad were removed. In this study species were categorized as strong when the S/N ratio was greater than 1.5, mostly to facilitate the inclusion of tracer species (e.g. Cu and Zn) with an S/N ratio between 1.5 and 2.0. See also Appendix A.2 for more information.

2.5.1 *Setting the total mass variable*

The total mass variable is used for post-processing the results and is classified as weak by default, therefore minimizing the influence on the outcome. In this case both the $PM_{2.5}$ and PM_{10} mass are included in the data set. Including both $PM_{2.5}$ and PM_{10} mass into the analysis poses an interesting question relating to the effects of including both on the outcome of EPA-PMF. We found that choosing either mass as total mass variable in EPA-PMF produces very similar results. For the sake of clarification we used PM_{10} as total mass throughout this report.

2.6 Adding additional uncertainties

All runs were performed with an added 'Extra Modelling Uncertainty' of 5%, which has been applied to all species, to take into account the errors which are not considered measurements or lab errors. Both measurements and lab errors are presented in the user-provided uncertainty files. Some issues that can cause modelling errors include transformation in the atmosphere and variation of source profiles. Generally at least 5% of extra modelling uncertainty seems to be appropriate (Norris et al., 2008).

2.7 Selecting the number of factors

The determination of the number of factors has been a much debated issue in the application of the PMF problem. Selecting the number of factors that will provide the best description of the dataset is always a compromise: too few factors will likely combine sources in one source profile, whereas too many factors will dissociate a real factor into additional but non-existing sources.

Currently there are several methods available which can aid in selecting the number of factors. More information about this subject is given in Appendix A.3.

In this study we used the scaled residual matrix (R) to aid in deciding the number of factors (Lee et al., 1999). We calculated IM, the maximum individual column mean, and IS, the maximum individual column standard deviation. In Figure 1, where IM, IS and Q_{ratio} (see also Mooibroek et al. 2011) are given, we are looking for a sharp drop for either IM or IS. If this drop cannot be observed, a range of number of factors must be evaluated by processing the data and examining the resulting profiles and the temporal variation of the individual contributions. The approaches described here for determining the number of factors can be helpful; however, there is no definitive indicator to determine the number of factors needed. In general, it still comes down to a judgment call made by the data analyst on whether or not the derived factors look reasonable.

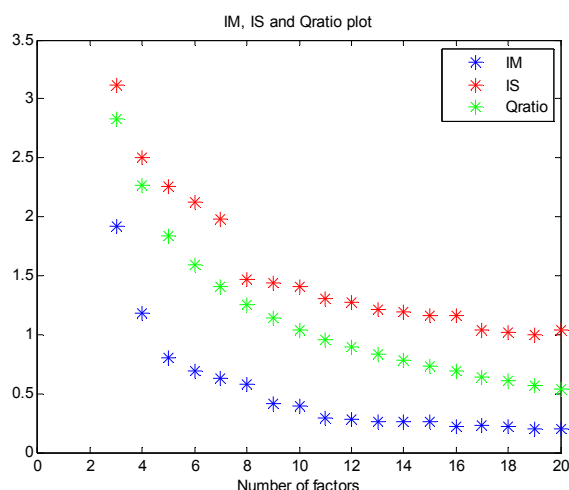


Figure 1 The behaviour of IM, IS and Q_{ratio} for each factor

A sharp drop in IS is observed after eight factors while IM is a bit inconclusive. We have evaluated the solutions with factors ranging from 6 till 9.

While evaluating the solutions for factors 6 through 9 we used the regression of total measured mass against the calculated contributions (G) matrix as another tool to aid in the selection of the number of factors. This regression produces scaling factors for each profile. These scaling factors have to be positive; negative factors could indicate too many factors have been used. The 6-, 7- and 8-factor solutions all produced positive scaling factors whereas the 9-factor solution contained negative scaling factors. Therefore the 9-factor solution probably contains too many factors and should not be considered an option.

The next step to determine the number of factors is to evaluate the calculated source profiles, looking at their composition and meaningfulness. Based upon a judgment call on whether or not the derived factors look reasonable we try to derive the best number of factors needed, starting with the 8-factor solution.

Looking at the 8-factor solution we can easily identify several profiles based on earlier work with these data (Mooibroek et al., 2011). These profiles are residual oil combustion (tracers: Ni, V), traffic and resuspended road dust (tracers: Cu, Fe, Al, Si, $PM_{2.5}$ EC), industrial (metal) activities/incineration (tracers: Zn), sea spray (tracers: Na, Mg, Cl), crustal material (tracers: Al, Si, Ti, Ca). Besides

these easily identifiable profiles, the 8-factor solution shows interesting behaviour. Like in the separate analyses of both fractions the results for the combined set show two separate secondary aerosol profiles: nitrate-rich and sulphate-rich. The odd thing is that almost no mass is apportioned to either $PM_{2.5}$ TM ($0.6 \mu\text{g}/\text{m}^3$) and PM_{10} TM ($0 \mu\text{g}/\text{m}^3$) in the sulphate-rich profile. A summation of the measured concentrations for each species in each fraction gives approximately $3 \mu\text{g}/\text{m}^3$. Based upon this observation there seems to be a discrepancy between mass apportioned by the model and the mass of the individual species.

The 8-factor solution also shows a split-up into two profiles driven by chloride. It seems the sea-spray factor dissolves into another factor containing an abundance of chloride, but nearly no other species related to sea-salt (e.g. sodium/magnesium). It seems there has been a split-up caused by Cl into a $PM_{2.5}$ and a PM_{10} component. Unfortunately the profile with an amount of chloride also shows traces of other tracers associated with industrial activities. In conclusion, the 8-factor solution seems to give interpretable results, but the lack of apportioned mass to the sulphate-rich profile is suspicious. While the composition of the source profiles makes sense, the contributions do not.

The first issue of the strange contributions of the two secondary aerosols profiles is not present in the 7-factor solution. Instead a combined profile with both nitrate and sulphate is observed. The chloride driven split-up as well as the other sources remain present.

The 6-factor solution takes care of the chloride driven split-up, resulting in a clearly identifiable sea-spray factor. The results are different from the exploration of the individual data sets in respect to finding only 6-factors instead of 7-factors. The individual data sets showed two different secondary aerosols, whereas the results are combined in this study. This might be caused the fact that the combined dataset contains a reduced set of measurements and possibly by the improved method of multiple imputation.

Based upon the evaluation of the 8-, 7- and 6-factor solutions we have decided to stick with the 6-factor solution. We do not have a reasonable explanation for the split-up in $PM_{2.5}$ Cl and PM_{10} Cl into two profiles when going from a 6-factor solution to a 7-factor solution. In this case the 6-factor solution yielded the most physical understandable results.

Another way of estimating the number of factors is by looking at the ratio (Q_{ratio}) between the $Q(\text{robust})$ value and the theoretical $Q(E)$. Ideally the Q_{ratio} should be close to unity, but in case the error estimates are not well determined this approach can be misleading. The 6-factor solution has a $Q(\text{robust})$ of 39107 compared to a theoretical $Q(E)$ of 25658 ($Q_{\text{ratio}}=1.52$) which points to a higher factor solution being more likely.

However, due to missing data and data below the detection limit a reasonable deviation of the $Q(\text{robust})$ value compared to the theoretical $Q(E)$ value is allowed. Based upon the physical understandable results for factor 6 we find the deviation between $Q(\text{Robust})$ and $Q(E)$ reasonable.

An additional 250 runs using random starting seeds were performed on the data set to ensure the convergence of the PMF problem. Typically the results with the lowest $Q(E)$ value are retained and processed further.

2.8 Rotational freedom

The use of constraints, like non-negativity, in the PMF model reduces the rotational freedom in the model, but does not ensure the found solution is unique. In theory there might be other (different) solutions which fulfil the model constraints as well. The PMF model contains a FPEAK parameter; using different values for this parameter allows us to explore the rotational freedom in the model by looking at changes in the $Q(E)$ value.

We performed several runs with different FPEAK values to gain more insight in the rotational freedom of the solution. It was found there was not much improvement over the central solution (FPEAK = 0) judging from the $Q(E)$ values. In this study we have used the 'central solution' for further processing and explanations. More information on the subject of rotational freedom can be found in Appendix A.4.

3 Interpretation of the 6-factor solution

3.1 Quality checks

Based upon the data pre-processing (e.g. multiple imputation) and the results we have performed several quality checks to ensure the validity of the results of the PMF analysis.

In the separate analysis (Schaap et al., 2010) we observed a strange behaviour of $PM_{2.5}$ and PM_{10} EC. By combining both fractions into one analysis we tried to eliminate this behaviour. However, while evaluating the preliminary results for the 6-factor solution (coincidentally as well as for the 7- and 8-factor solution) we still observed the strange behaviour of $PM_{2.5}$ EC and PM_{10} EC.

3.1.1 *$PM_{2.5}$ EC and PM_{10} EC behaving differently*

As in the separate analysis (Schaap et al., 2010) it seems that $PM_{2.5}$ EC is associated with a different factor than PM_{10} EC, something one would not expect. Ten Brink et al., (2009) did some research at the carbon (EC/OC) concentrations found in the BOP programme. The authors mention that in general about 90% of the EC was present in $PM_{2.5}$ with the exception of Vredepeel where a substantial amount of EC was found in the coarse fraction. This behaviour might be the underlying source of the unexpected split up between $PM_{2.5}$ EC and PM_{10} EC using PMF.

To establish the effect of the EC behaviour at Vredepeel we have removed all sample days from Vredepeel and ran an indicative PMF analysis on the remaining data set.

Comparing the calculated factor profiles with the results of the data set including Vredepeel shows that the majority of apportioned $PM_{2.5}$ EC still is associated with a different profile than the one containing the majority of apportioned PM_{10} EC. This leads to the conclusion that the strange behaviour of both $PM_{2.5}$ and PM_{10} EC is not related to suspected strange EC measurements at Vredepeel. The strange behaviour reported by Ten Brink et al. (2009) also does not seem to have a significant influence on the PMF analysis results.

3.1.2 *Influence of multiple imputation*

It is possible the strange behaviour of $PM_{2.5}$ EC and PM_{10} EC is caused by the multiple imputation (MI) which was used to fill the gaps in the data set. After all, approximately 33% of both $PM_{2.5}$ EC and PM_{10} EC were missing.

To establish the effect of MI on the EC behaviour we have constructed a data set in which all imputed values were removed, leaving a data set containing only measurements. We have compared the source profiles of the 6-, 7- and 8-factor solutions to assess the influence of multiple imputation.

Compared to the imputed set there are some slight differences. The 6- and 7-factor solution show similar composition of the source profiles for both data sets. For the 8-factor solution the results are also very similar, the sea spray factor, a factor with an abundance of Cl and both sulphate-rich and nitrate-rich secondary aerosol are clearly identifiable. Whereas the imputed set had almost no $PM_{2.5}$ or PM_{10} mass apportioned, the measured set shows at least some mass is

apportioned for PM_{2.5} (1.54 µg/m³) and PM₁₀ (2.24 µg/m³). The phenomenon is most likely caused by the rotational freedom in the PMF solution and the differences in sample size for both data sets.

The split up between PM_{2.5} EC and PM₁₀ EC still occurs in this data set, indicating that the influence of the multiple imputation method to estimate the missing values on this behaviour is probably limited.

Comparing the measured data with both measured and imputed data shows that there is a lot of similarity between the found source profiles. As expected and seen earlier in the correlation analysis there are some slight differences in the apportionment of the species which are likely caused by the different sample size and/or rotations and/or imputation of missing values for these components, most notably OC/EC/SIA.

We therefore conclude that there is a very limited influence of the use of multiple imputation to fill in the missing data for this data set.

3.2 Identification of the factor profiles

In this section we will examine the source profiles for the 6-factor solutions more closely based on the existence of chemical constituents and compare the results with the results published earlier (Mooibroek et al., 2011).

The order of the unknown sources was established on the average contribution of a specific PM₁₀ source on the total mass on all available sites.

Figure 2 shows the calculated source profiles with both contributions of PM_{2.5} species (blue) and PM₁₀ species (green). For comparison these contributions are displayed on a log-scale (left y-axis). The red dots denote the percentage of the apportioned average mass for this species is present in this profile (right y-axis). Species with high percentages in a profile are considered dominant species for that profile and are used to identify possible real-life source types.

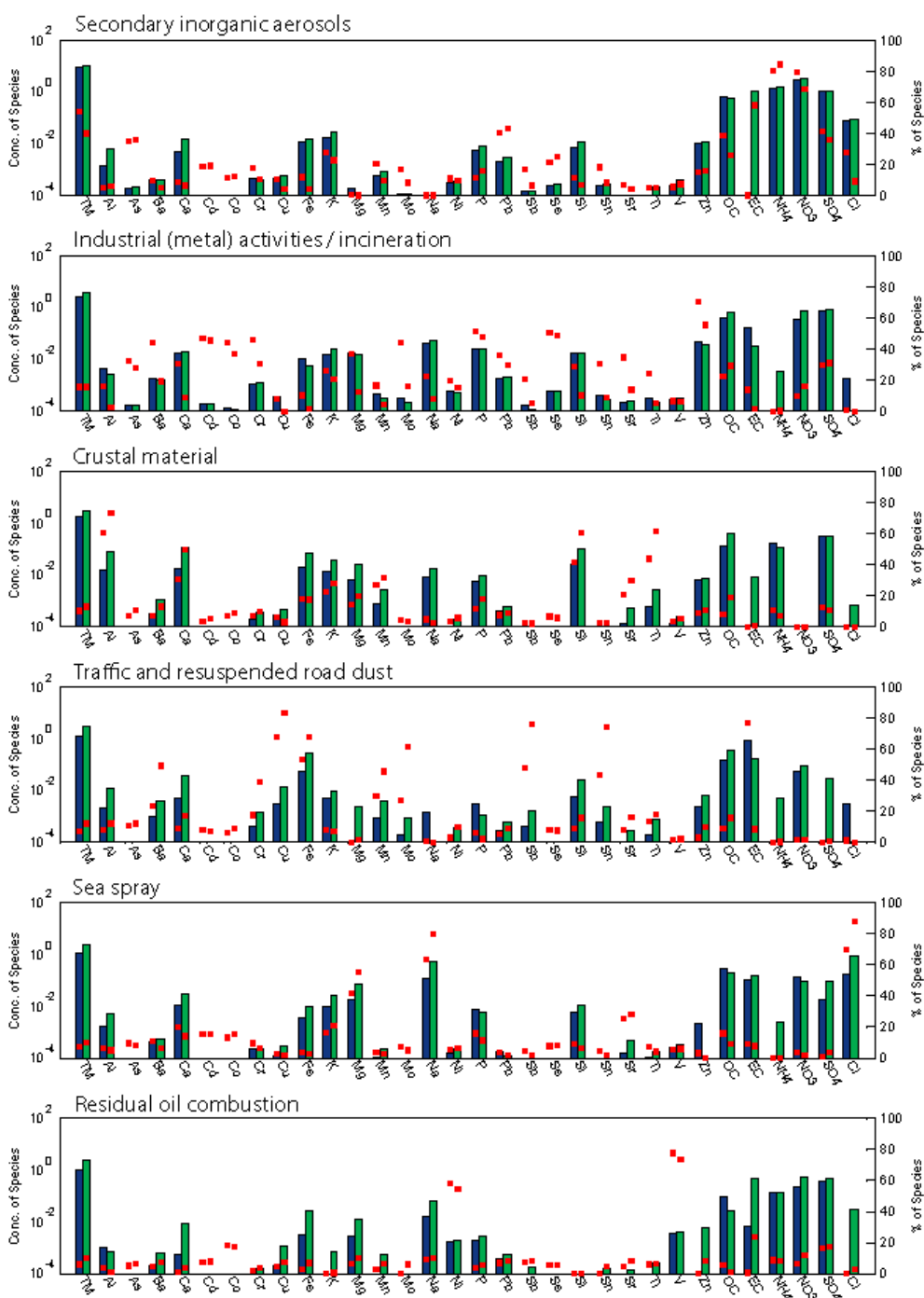


Figure 2 Calculated source profiles for $PM_{2.5}$ (blue) and PM_{10} (green). The red dots indicate the relative contribution (%) of the profile to the total mass of each component. Note that, in terms of percentage, a small contribution may be associated with a larger mass contribution rather than with a large relative contribution, depending on the respective concentrations. The bars indicate the associated contribution in mass units, shown here on a logarithmic scale.

Factor 1 (secondary inorganic aerosol) consist mainly of the secondary aerosols in both fraction (ammonium, nitrate, sulphate aerosol). Earlier work (Schaap et al., 2010 and Mooibroek et al., 2011) showed a split-up between a sulphate and a nitrate component for secondary aerosol. The factor also contains some OC and surprisingly a large amount of PM₁₀ EC.

Previous studies show that carbon and tracer elements typically become associated with the secondary sulphate-rich aerosol in both the fine and coarse fractions (Ramadan et al., 2000; Song et al., 2001; Kim et al., 2003; Lui et al., 2003). Other studies also show a correlation of OC with some EC for a secondary nitrate-rich profile (Lee et al., 2006 and Kim et al., 2003). Furthermore, OC is considered to be semi-volatile, similar to ammonium nitrate (Schaap et al., 2010).

All measurements in the BOP study were performed by one method but recent research has shown the split-up between EC and OC is different compared to other methods. The various techniques can give values for EC that differ by a factor of two to three. The measurements of total carbon (EC+OC) showed a good agreement (Ten Brink et al., 2009).

A recent study by Bae et al. (2009), in which two common thermal-optical carbon methods were compared, could give some pointers towards the explanation of the strange behaviour found for EC. While an excellent agreement for total carbon (i.e. the sum of EC and OC) was observed, differences in the split between the measured EC and OC were found. The EC difference between the methods had a moderate positive correlation with indicators of secondary organic aerosol and sulphate. The researchers also observed a different behaviour in seasonal relationships (Bae et al., 2009).

It is possible the positive correlation with the indicators of secondary aerosol is primarily observed for PM₁₀ EC in this study, leading to the inclusion of PM₁₀ EC in the secondary organic aerosol profile. However, little difference between the PM_{2.5} and PM₁₀ concentrations was found, making it even more difficult to understand the difference between PM_{2.5} and PM₁₀ EC in the PMF analysis.

A seasonal pattern for secondary nitrate-rich aerosol is expected as temperature greatly affects the equilibrium of ammonium nitrate, ammonia, and nitric acid. Low temperature during winter favours the formation of the particulate form. On the other hand secondary sulphate-rich aerosol shows slightly higher source contributions during the summer.

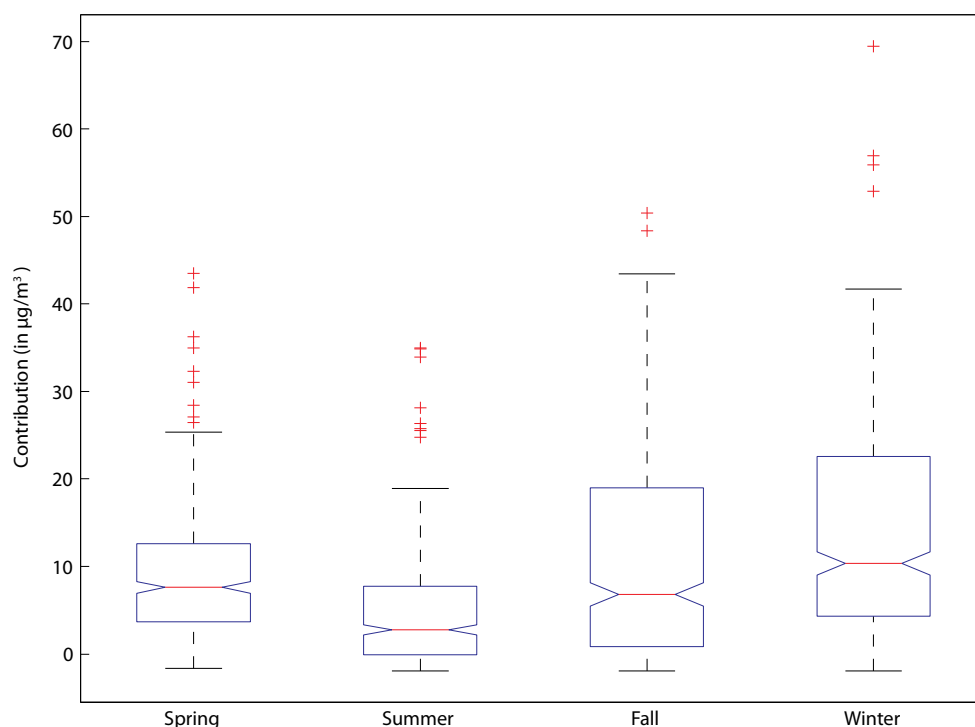


Figure 3 Seasonal PM₁₀ contributions for the factor identified as 'Secondary inorganic aerosol'

Based upon the seasonal patterns of this factor, secondary nitrate-rich aerosol dominates the source contributions of this profile. This corresponds well with the results presented by Schaap et al. (2011) where the contribution of a nitrate-rich secondary profile was on average 36% on all sites whereas the contribution of the sulphate-rich secondary profile was approximately 18%.

Factor 2 (industrial (metal) activities/incineration) contains high amounts of various metals which could not be identified as a single source. High concentrations of zinc are mainly contributed by industrial activities such as mining, coal and waste combustion, and steel processing (Marcazzan et al., 2001). Zinc is also used in the rubber or painting industry (Salminen et al., 2005). Chromium (major component used in coating steel), cobalt (coal combustion and special steels), arsenic (coal combustion, geothermal powerplants and sulphidic ore roasting and smelting), strontium (industrial waste from Zn refineries and disposal of incineration ash and coal ash) are all highly associated with either coal combustion or steel/metallic industrial activities (Salminen et al., 2005). Other studies (Pacyna, 2001; Song et al., 2001) attribute zinc, lead, nickel, copper and arsenic a lot to the municipal solid waste incineration and non-ferrous metal smelting. Combustion of fossil fuels (coal) is also considered to be a contributor of nickel, copper, arsenic and zinc (Lee et al., 1999).

The main sources for calcium are cement factories, dust and fertilizers. Phosphorous, potassium, magnesium and cobalt are also associated with fertilizers (Salminen et al., 2005). Additionally some calcium, magnesium and iron in this factor might have been contributed by fly ash from combustion (Liu et al., 2002). Based upon the elemental composition of this source, it seems to be a mixture of various sources, not limited to municipal solid waste incineration, (coal) combustion, metallic industrial activities and fertilizers.

The profile, as shown in Figure 2, also contains some nitrate and sulphate aerosol, suggesting at least part of this source could be considered large scale.

Factor 3 (crustal material) contains the typical elements of crustal material (particularly silicon and aluminium, but also calcium and iron). It also includes some organic carbon (OC), as is reported by many authors (Lewis et al., 2003; Lee et al., 2006) and points to detritus from vegetation and other organic soil constituents. Factor 3 is categorized as 'crustal material (CRM)'.

Seasonal analysis for crustal material show the highest contributions during the spring period. Especially at agricultural sites this behaviour is expected. During spring farmers generally prepare the soil by ploughing which can lead to high concentrations of dust when the weather conditions are dry.

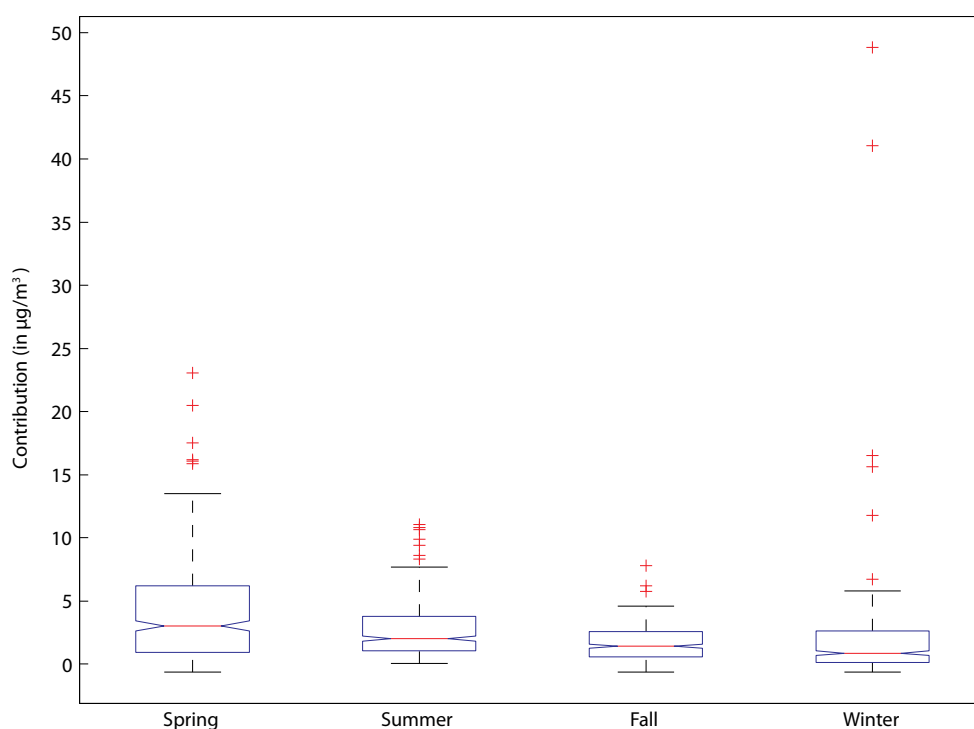


Figure 4 Seasonal PM_{10} contributions for the factor identified as 'Crustal material'

Factor 4 (traffic and resuspended road dust) is made up mainly of $PM_{2.5}$ elemental carbon (EC), and a small amount of organic carbon (OC), and some crustal material (Al, Si, Ti). As with the results of the individual data sets (Schaap et al., 2010) the lack of PM_{10} EC is suspicious, especially with a large part of $PM_{2.5}$ EC apportioned to this source. The large contribution of $PM_{2.5}$ EC, with EC considered to be originating as primary emissions, along with some iron and copper, suggests that factor 4 can be labelled as traffic emission, both a mixture of petrol and diesel exhaust. Several studies have linked high concentrations of copper to diesel emissions (Swietlicki et al., 1996) or from wearing of vehicle breaks (Sternbeck et al., 2002, Laschober et al., 2004). Reasonably high concentrations of iron, aluminium, silicon and manganese (considered crustal elements) suggests dust resuspended by traffic, although a portion of the found iron might also be caused by brake dust (Hildemann et al., 1991) and heavy-duty diesel emissions (Ramadan et al., 2003). It is not surprising that crustal material (CRM) is included in this factor, as traffic is a

strong urban source of resuspension of dust particles. Besides the presence of manganese in crustal material anthropogenic sources include both traffic and industrial activities (Salminen et al., 2005). Molybdenum is used as an additive in lubricants and is also released in the environment from the combustion of fossil fuels, explaining the contribution of molybdenum in this factor (Salminen et al., 2005).

Several other studies detail with the use of barium as a specific tracer for traffic (e.g. Fernández-Espinosa and Ternero-Rodríguez, (2004) or Monaci and Bargagli (1996)). Judging from the results for factor 4 presented in Figure 2, barium seems to be a more specific tracer as a PM_{10} component compared to a $PM_{2.5}$ component. Harrison et al. (2003) showed by using NO_x and particle count as tracers of road traffic emissions, the elements copper, zinc, molybdenum, lead and barium show significant correlations indicative of a traffic source contribution. The authors also found that the correlation with barium improved when comparing the results of the PM_{10} fraction with the $PM_{0.2}$ fraction, indicating association of barium with very fine particles. However, the result of EPA-PMF 3.0 in this study suggests the majority of the barium concentrations associated with traffic related emissions is found in the PM_{10} fraction. Similar results for barium was found by Schaap et al. (2011) in the separate analysis of both data sets.

Examination of the weekday/weekend contributions shows that the highest contributions of this profile occur on weekdays.

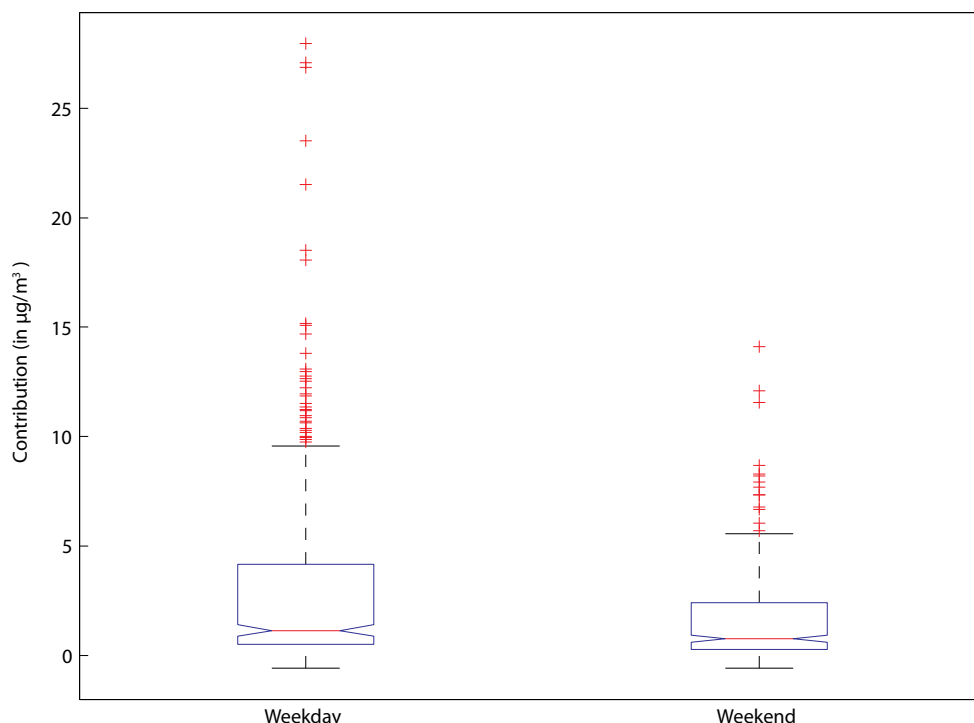


Figure 5 Weekday and weekend contributions for the factor identified as 'traffic and resuspended road dust'

Factor 5 (sea spray) contains the greatest proportion of the sea salt aerosol elements (sodium and chloride) of all the factors. The traces of magnesium, potassium and calcium are mainly associated with the sea salt particles. However, the lack of sulphate in both $PM_{2.5}$ and PM_{10} is conspicuous and also

observed by Schaap et al. (2011). The label for factor 5 is categorized as 'sea spray'.

The chloride/sodium ratio of both $PM_{2.5}$ (1.6) and PM_{10} (1.6) correspond well with the chloride/sodium ratio of uncontaminated sea water (1.8; Binas). The ratio between chloride and magnesium is lower than the ratio found in uncontaminated sea water.

An explanation for the slightly lower ratios involving chloride is a phenomenon called chloride depletion. While travelling in air chloride can be removed from sea salt aerosol by reactions with both HNO_3 and H_2SO_4 and in both cases chloride becomes associated with the gaseous HCl. Chloride depletion is also depended on the time the sea salt aerosol is airborne and therefore correlated with the distance travelled. Sodium and magnesium are more stable in the atmosphere and are better tracers for sea salt than chloride.

However, the sodium and magnesium ratio of both $PM_{2.5}$ and PM_{10} are comparable to uncontaminated sea water, but in general lower. A possible explanation for this is that another factor also contains both sodium and (more) magnesium but no chloride (due to the depletion process).

The contribution of this factor on all sites is the highest during the winter period as can be seen in Figure 7. This corresponds well with the finding by Manders et al., 2009 that the highest sea salt concentrations were found during the fall and winter periods. These periods are considered to be the windy seasons with large low pressure systems over the Atlantic Ocean and the North Sea.

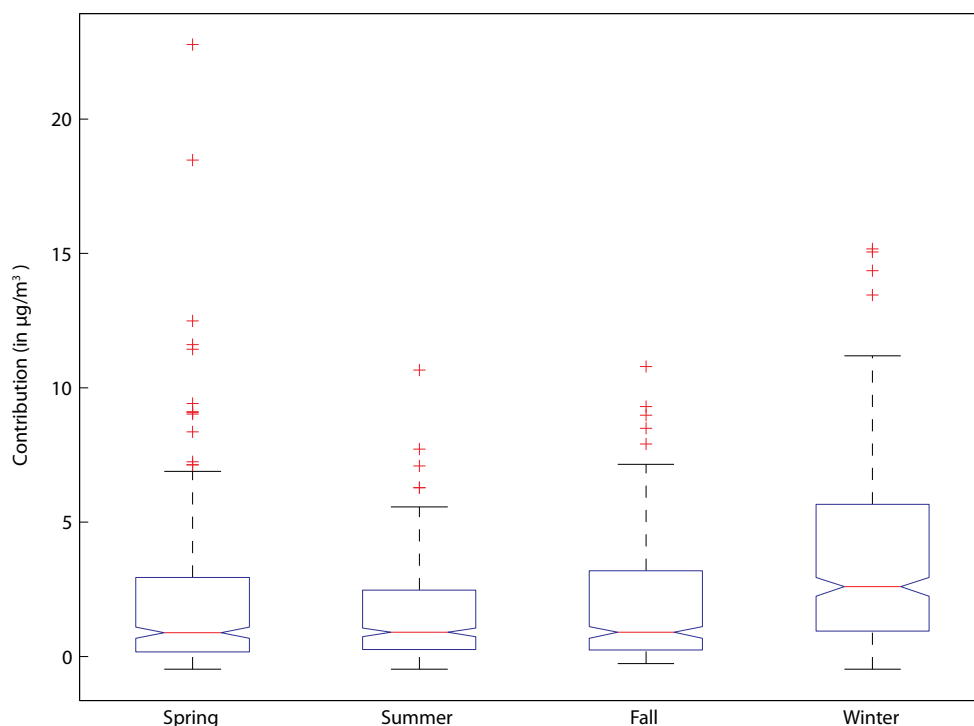


Figure 6 Seasonal PM_{10} contributions for the factor identified as 'Sea spray'

Factor 6 (residual oil combustion) contains the tracers for oil combustion and incineration, vanadium and nickel. Typically oil combustion sources are

ships in harbours and along the coast, municipal district heating power plants and industrial power plants using heavy oil. A recent study by Vallius (2005) showed inland shipping via canals can also be considered a source of particulate matter. For both fractions the source profile also contains some sea salt aerosol elements (sodium and magnesium), however chloride is only slightly apportioned in PM_{10} . This could explain the lower ratios found for chloride and magnesium as well as sodium and magnesium in the sea salt profile.

Furthermore, a small amount of nitrate and sulphate aerosol is found in this profile. In other studies, this factor is not always part of the suite of source profiles. Factor 6 is categorized as 'residual oil combustion'. Considering some of the species in the profile are primarily transported over a long range, this would suggest some of the contribution from the residual oil combustion is offshore.

3.3 Checking the apportioned mass against measured mass

Several different methods, each with their own assumptions, exist that allow us to compare the apportioned mass by the model with the measured mass. More details about these methods and their associated assumptions can be found in Appendix A.5.

In this study we specified the total measured PM_{10} mass as a 'Total variable (TM)' in EPA-PMF 3.0. This variable will be used by the GUI in the post-processing results. Because the total variable should not have a large influence on the solution it is given a high uncertainty by categorizing the TM as a weak variable. A significant advantage of this is that EPA-PMF tries to distribute the measured PM_{10} mass over each calculated profile, effectively providing the total PM_{10} mass associated with the profile. Additionally we also included the $PM_{2.5}$ total mass, setting this variable as a weak variable as well. This also provides us with the distributed $PM_{2.5}$ mass over each calculated profile.

We used both the apportioned $PM_{2.5}$ and PM_{10} mass as the scaling constants to transform the contribution matrix to concentration units. This approach gives us information about the contributions of each profile to each of the PM fractions. These contributions for both mass fractions can be summed up to give the predicted total mass for that fraction for each sample, and this latter value can then be compared with the measured mass for that particular fraction.

When performing this comparison we assume that all unmeasured species add negligible mass to the profiles (e.g. the measured species account for 100% of the mass). In theory we would observe a near to perfect 1-1 line, but in reality the measured species generally account for 75-95% of the total mass.

By making a simple plot of the predicted mass versus the measured mass and calculating the correlation coefficient, we are able to determine whether the 6-factor model used in this case accounts for an accurate description of the total measured PM mass. The Pearson's pair-wise correlation coefficients for the 6-factor model are 0.8984 and 0.8649 for the $PM_{2.5}$ and PM_{10} mass, revealing that this model indeed describes the apportionment of measured mass from both to sources reasonably well. The correlation coefficients correspond well to the results from the Bronstoft study (Bloemen et al., 2008) and the separate analysis of both $PM_{2.5}$ and PM_{10} (Schaap et al., 2010).

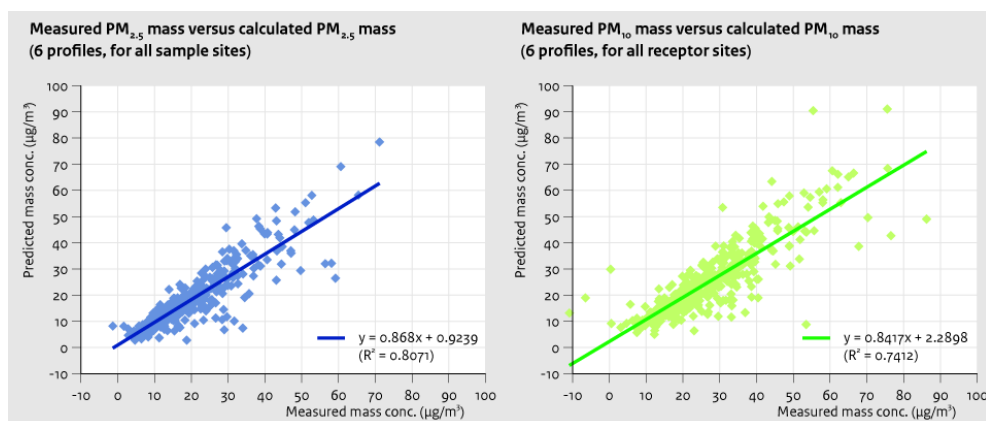


Figure 7 Comparison of measured mass and apportioned mass at all six receptor locations for both $PM_{2.5}$ (left, in blue) and PM_{10} (right, in green) data sets, based on the contributions of all six factors
The solid lines are the linear regression results.

3.4 Comparison apportioned mass against mass closure

The PMF generates time and composition profiles. Regression of the time profiles with the real weighted $PM_{2.5}$ mass shows the relative importance of each profile. Comparing this regression result to the summation of the component contributions in the profile shows which profiles are associated with missing mass. In the summation of the components the metals were expressed as their oxides following Schaap et al. (2010). Furthermore it was established the total carbonaceous mass (TCM) needs to have a factor 1.3 applied (Ten Brink et al., 2009). Due to the fact we don't use the TCM, but the split-up in EC and OC, we have applied the 1.3 factor to both EC and OC.

Table 2 Mass closure for the $PM_{2.5}$ data set based upon the sum of selected species (after applying a correction factor for several species) compared to the mass apportioned by PMF to each source

Profile	PMF apportioned mass ($\mu\text{g}/\text{m}^3$)	Sum species mass ($\mu\text{g}/\text{m}^3$)	Ratio
Secondary aerosol	9.0821	6.2014	0.68
industrial (metal) activities/incineration	2.6462	2.1149	0.80
crustal material	1.7363	0.9290	0.54
traffic and resuspended road dust	1.2699	1.5739	1.24
sea spray	1.1778	1.0443	0.89
residual oil combustion	1.0203	0.9368	0.92
sum over all profiles	16.9326	12.8004	0.76

Comparing these results show that the $PM_{2.5}$ secondary inorganic aerosol and $PM_{2.5}$ crustal material factor all have a relatively low ratio of (below) 0.7. This indicates that these factors apparently contribute more to the weight than the sum of the analysed chemical constituents. In case of secondary inorganic aerosol this is consistent with the quite likely hypothesis these hygroscopic components particularly associate a relatively large amount of water.

PM_{2.5} crustal material does not contain any hygroscopic components; therefore the low weight contribution from the sum of the chemical constituents could not be attributed to water. However, the 'PM_{2.5} traffic and resuspended road dust' has a large ratio and also contains some contributions of PM_{2.5} crustal material. It might seem that contributions of tracers related to PM_{2.5} crustal material are perhaps underestimated in the crustal material profile and overestimated in the traffic and resuspended road dust profile. We compared the ratios of Al, Ca, Si and Ti for both profiles hoping to identify the species which are overestimated. However, the ratios between those species did not change much in both profiles, indicating there was not an overestimation of the contribution of these species in the PM_{2.5} crustal material or PM_{2.5} traffic and resuspended dust profile.

It could also be possible that PM_{2.5} EC contribution in the traffic and resuspended road dust profile is responsible for the overestimation of mass by summing the species. Due to the expected nature of EC in general we assumed PM₁₀ EC being the species behaving oddly, but perhaps both PM_{2.5} and PM₁₀ EC are behaving oddly in some way.

Other PM_{2.5} components more or less have a unity factor which corresponds with their chemical nature. The same analysis was also performed for the PM₁₀ components, for which the results are shown in Table 4.

Table 3 Mass closure for the PM₁₀ data set based upon the sum of selected species (after applying a correction factor for several species) compared to the mass apportioned by PMF to each source

Profile	PMF apportioned mass (µg/m³)	Sum species mass (µg/m³)	Ratio
Secondary aerosol	9.6484	8.37148	0.87
industrial (metal) activities/incineration	3.7422	2.87843	0.77
crustal material	3.1286	2.08490	0.67
traffic and resuspended road dust	2.9393	1.56570	0.53
sea spray	2.3823	2.31738	0.97
residual oil combustion	2.3386	2.05027	0.88
<i>Sum over all profiles</i>	<i>24.1794</i>	<i>19.26816</i>	<i>0.80</i>

For PM₁₀ we see an underestimation for the traffic profile, probably caused by the lack of EC in PM₁₀. It is strange that EC has to turn up somewhere else and most likely should lead to an overestimation of the total mass of that factor. A large portion of PM₁₀ EC turns up in the secondary aerosol profile, which has indeed a higher ratio than one would expect based on the hygroscopic nature of secondary aerosol.

Compared with the results of the previous study it can be seen that the sea spray ratio is somewhat higher than expected. Both the separate analysis for PM_{2.5} and PM₁₀ showed a lower ratio for sea spray, in line with the hygroscopic nature of the species associated with this profile.

The mass closure for sea salt in the separate analysis (Schaap et al. 2010) is more conclusive. The effects observed in this study are probably caused by the combining of both fractions.

4 Evaluation of the PMF results for each sample site

Due to the similarities of the sources (each site has different contributions of the same source types) we have chosen to discuss the evaluation of only one site in the main text of this document. The other sites are evaluated in the appendixes.

First we will discuss the results for the site Schiedam. Next to the contributions of each source we will try to identify days with high contributions from different sources. Using the HYSPLIT model an attempt is made to discover the origin of these high contributions. For example, during the evaluation of the results a global phenomenon, contribution of dust originating from the Saharan desert, was found on all receptor sites and is discussed in more detail in the HYSPLIT section.

4.1 Schiedam

The characteristics of the sites are described elsewhere in detail (Schaap et al., 2010). The location of Schiedam is considered to be an urban background site located in the West of the Netherlands in the Rotterdam agglomeration. Rotterdam has approximately 600,000 habitants and is predominately influenced by refineries and harbour related activities.

4.1.1 Time series contributions

The time series contribution plots for the six profiles are given for both data sets in Figure 8. Besides giving information about certain events on several days for the sources, the plots also give some information about the contributions of each source in each mass fraction. If the time series of each mass fraction for a specific source are more or less similar this might indicate the majority of the contribution from this fraction can be found in the $PM_{2.5}$ fraction. For example, in the plot below the lines for both $PM_{2.5}$ and PM_{10} are similar in the factor labelled 'secondary aerosol'. This might be an indication this source is primarily found in the $PM_{2.5}$ fraction and not in the $PM_{2.5-10}$ fraction. Another example is the 'sea spray' and 'crustal material' factor. Although there seems to be a fair amount of both sources in the $PM_{2.5}$ fraction, it is likely the majority of the contributions from both sources can be found in the $PM_{2.5-10}$ fraction.

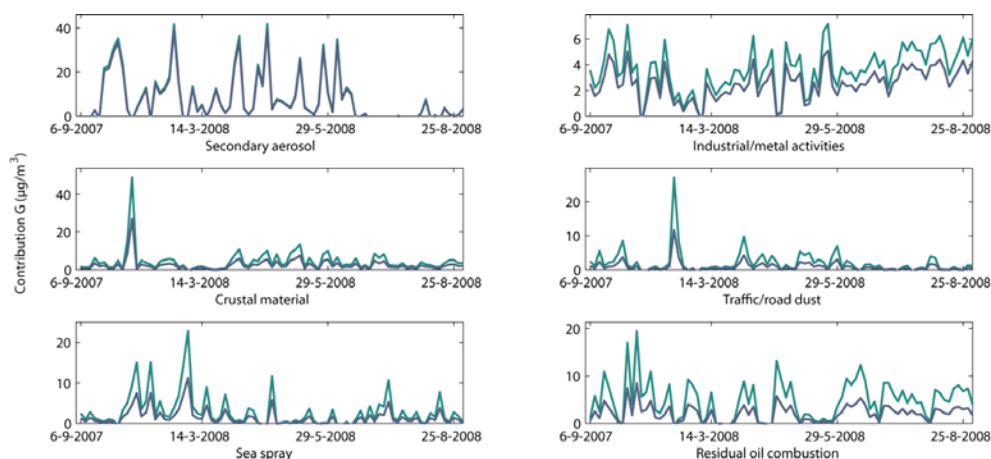


Figure 8 Time series contribution plots for six source profiles for the location at Schiedam

The blue line represents the results for $PM_{2.5}$ and the green line for PM_{10} .

Comparing the contributions with the result of the study by Schaap et al. (2010) shows a similar behaviour. For example the crustal material profile shows a high contribution between 23rd January and 25th January 2008. In the separate analysis this contribution was identified as a peak caused by a Saharan dust episode. More detailed information on the analysis related to this high contribution of crustal material can be found in Schaap et al (2010) and Mooibroek et al (2011).

4.1.2 Conditional probability plots

The Conditional Probability Function (CPF) was used to determine the directions in which sources are likely to be located. The CPF was calculated using the source contributions (G) from the PMF analysis and the wind direction values measured on a meteorological station nearby. For the location Schiedam the nearest meteorological station is KNMI station 344, Rotterdam Airport. To match the hourly wind data each daily contribution was assigned to each hour of a given day, as proposed by Kim et al., 2003. More information about the underlying mathematics of the CPF can be found in Appendix A.6.

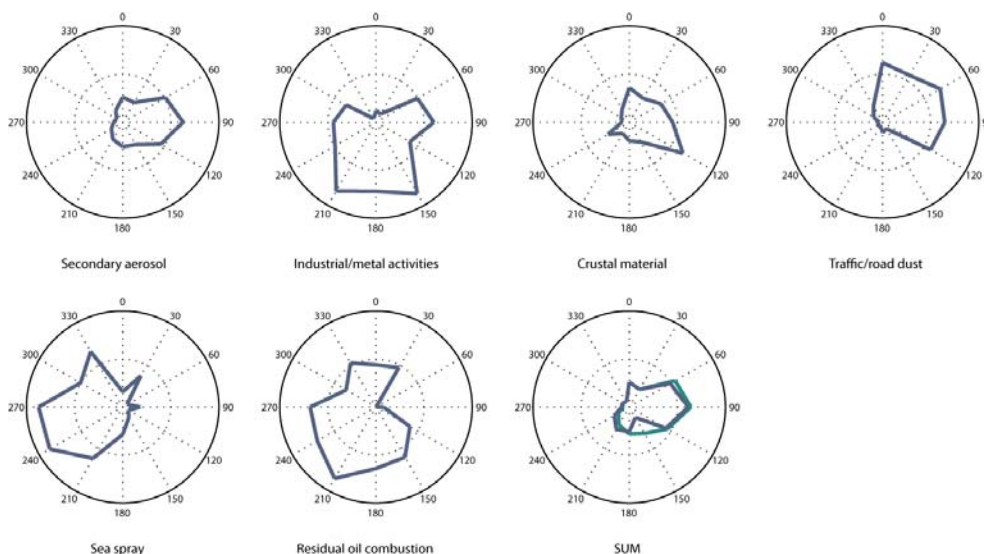


Figure 9 CPF plots for the six source profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport. The blue line represents the results for $PM_{2.5}$ and the green line for PM_{10} .

As can be seen in Figure 9 the contribution from the industrial (metal) activities/incineration source seems to be coming predominately from the south-east and south-west. Since the receptor is located in an industrial area, the suggested source direction is not unlikely.

The CPF plot for the traffic-related source show contributions are from the north-east of the receptor site. Similar behaviour is found for the crustal material and the profile containing the secondary inorganic aerosol. A large contribution to the secondary inorganic aerosol profile is expected from the east, as opposed to the relatively clean air coming from the west. Furthermore, a large industrial area is located at the east of the sample site in Germany. The contribution of sea spray is found in the south westerly direction, most likely from the North Sea, which is expected.

Contributions for the residual oil combustion are coming from west-southwest from the receptor site, but a dominant source might also be located in the northwest direction. In the south westerly direction the contributions seems to be coming from the 'Botlek/Pernis' area.

The highest contributions to the PM mass are caused by source contributions located in the easterly direction of the sample site Schiedam.

4.1.3 Comparison of apportioned mass against measured mass

Figure 11 shows the comparison between the daily reconstructed fine mass contributions from the six sources with the measured fine mass concentrations. For $PM_{2.5}$ the Pearson's pair wise correlation coefficient is 0.8831 and the reconstructed contributions agree well with the measured contributions. For PM_{10} the Pearson's pair-wise correlation coefficient is 0.8807 and similar to the $PM_{2.5}$. The reconstructed contributions again correspond well with the measured contributions.

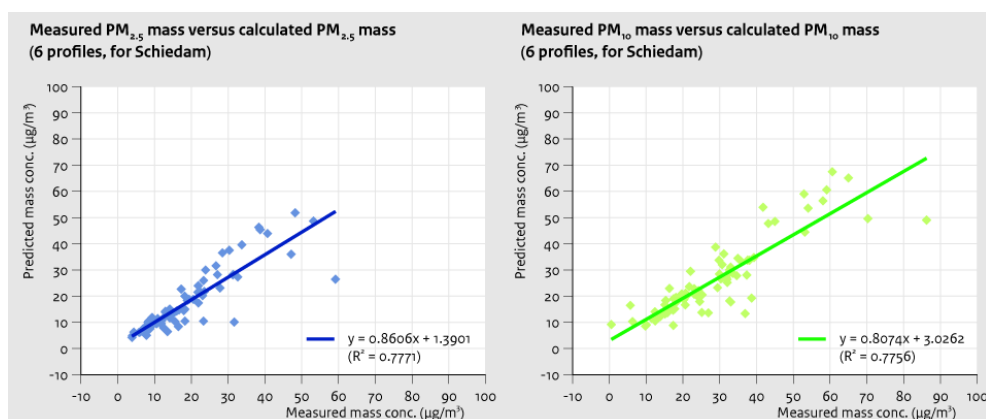


Figure 10 Comparison of measured mass and apportioned mass at Schiedam for both $PM_{2.5}$ (left, in blue) and PM_{10} (right, in green) data sets, based on the contributions of all six factors

The solid lines are the linear regression results.

4.1.4 Calculated source contributions

For each of the sample sites the source contributions of the seven identified sources were calculated and are given in the figures below. To make it easier to compare the source contributions the order of the sources for both fractions are kept the same.

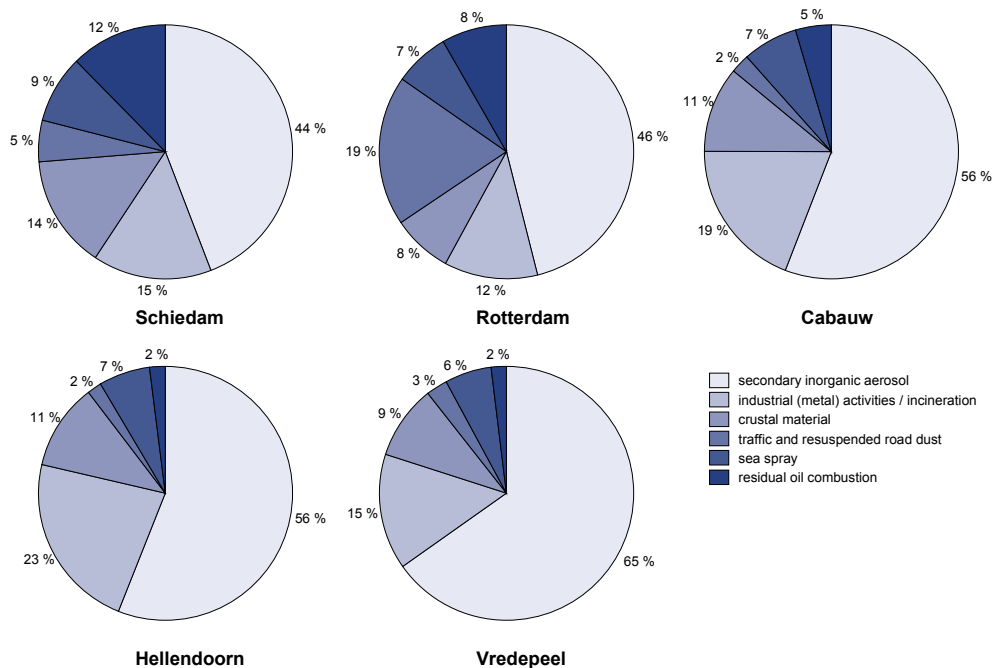


Figure 11 Source apportionments for $PM_{2.5}$ at selected locations (top left diagram is urban background, mid-top diagram is traffic-related and the remaining diagrams are rural background locations)

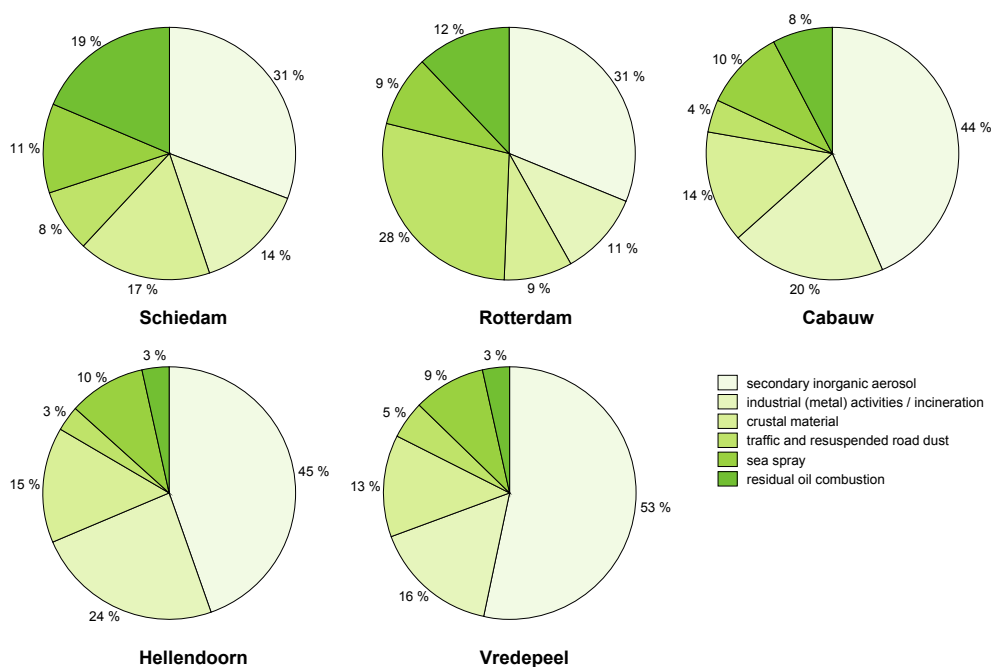


Figure 12 Source apportionments for PM_{10} at selected locations (top left diagram is urban background, mid-top diagram is traffic-related and the remaining diagrams are rural background locations)

4.1.5 $PM_{2.5}$ and PM_{10} mass contributions of each source type at each site

Tables 5 and 6 show the average mass contributions of each source type at the five different locations. We also have given the summation of each average to establish the average PM concentration of the site.

When we compare the average contribution on each site with the average PM mass for the sample days used in the analysis we see that in most cases the PMF analysis slightly underestimate the contributions. Despite this slight underestimation the found mass contributions from PMF are in good agreement with the measured contributions.

The contributions mentioned in Table 5 will differ from the contributions established in the separate analyses due to a different sample size of the data set used in the analysis. This will make absolute mass comparison between the results found in this study and by Schaap et al. (2010) difficult.

Table 4 Mass contributions per site per profile $PM_{2.5}$ in $\mu g/m^3$

	Schiedam	Rotterdam	Cabauw	Hellendoorn	Vredepeel
Secondary aerosol	7.43	8.59	8.86	7.14	12.21
Industrial/metal	2.55	2.22	3.03	2.88	2.76
Crustal material	2.43	1.42	1.72	1.40	1.76
Traffic/road dust	0.88	3.57	0.39	0.24	0.51
Sea spray	1.45	1.32	1.11	0.83	1.11
Oil combustion	2.08	1.54	0.73	0.26	0.37
SUM source types	16.82	18.66	15.84	12.75	18.72
Measured TM	18.0	20.0	18.4	14.5	19.7

Table 5 Mass contributions per site per profile PM_{10}

	Schiedam	Rotterdam	Cabauw	Hellendoorn	Vredepeel
Secondary aerosol	7.89	9.13	9.41	7.58	12.97
Industrial/metal	3.60	3.13	4.29	4.07	3.90
Crustal material	4.38	2.56	3.10	2.52	3.18
Traffic/road dust	2.05	8.26	0.90	0.55	1.18
Sea spray	2.93	2.66	2.24	1.68	2.25
Oil combustion	4.77	3.53	1.67	0.59	0.84
SUM source types	25.62	29.27	21.61	16.99	24.32
Measured TM	28.0	31.2	21.6	19.9	26.2

4.2 COD analysis

In general the contributions of all factors show a consistent picture over all sites. To further address the spatial distribution of the calculated source contributions we have calculated the coefficients of divergence (COD). Primarily used in numerical analysis of ecological data the COD is a coefficient used to determine the resemblance between objects or the variables describing these objects. Several studies have used the COD to provide information on the degree of uniformity of source profiles between monitoring sites (Kim et al., 2005; Kim and Hopke, 2008). For the spatial distribution the COD approaches zero if the source contributions at the two sites are similar. In case the source contributions are very different the COD approaches unity. The calculated COD for PM_{10} is shown in Figure 13 (note – the figure for $PM_{2.5}$ is the same since the underlying spatial distribution is the same).

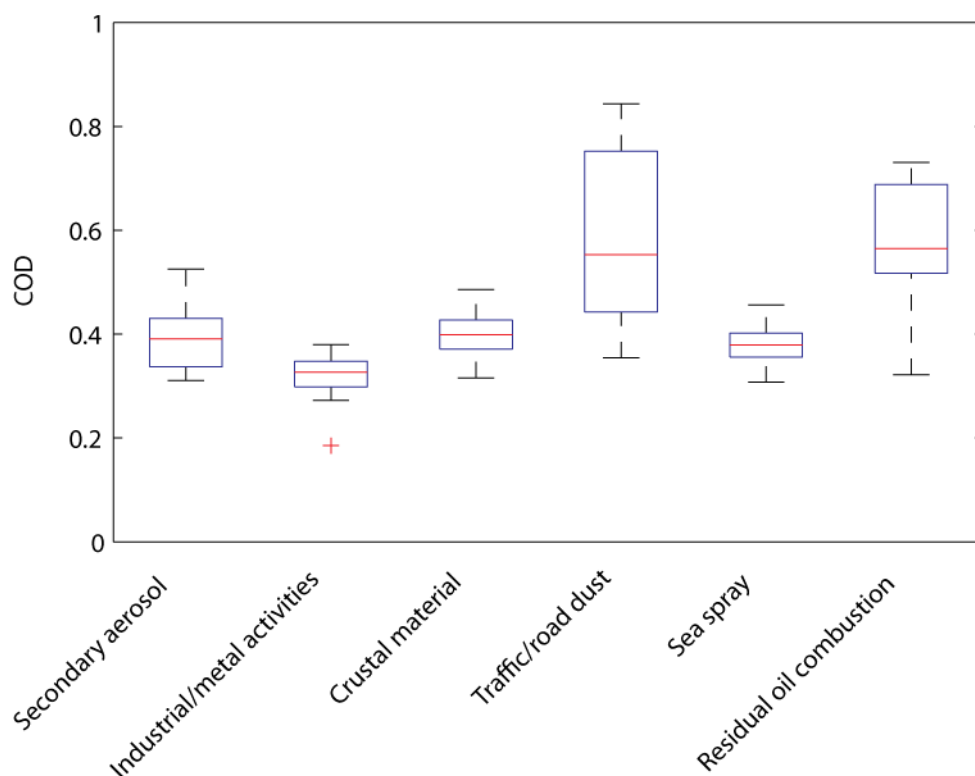


Figure 13 Coefficients of divergence (COD) for identified PM sources, obtained from five sample sites

All combinations of sites yield almost the same low COD for secondary inorganic aerosol. This behaviour has not only been found in the previous study (Mooibroek et al., 2011), but also by several previous studies (Kim et al., 2005 and Kim and Hopke, 2008). The importance of long-range transport into and across the monitored area is reflected in the small spatial variability. In the previous study it was found that the nitrate component of secondary aerosol also showed a relatively small spatial variability on average. The COD for nitrate tends to increase as function of distance. Hence, the highest COD value for the secondary inorganic aerosol was found between Hellendoorn and Schiedam (0.53). This behaviour corresponds well with the results of the previous study.

As expected, a significantly larger spatial variability is found for the traffic factor with the largest CODs between the urban/street sites and the rural sites. Interestingly, the low COD values between the rural sites indicate that the source contribution on these sites behaves similarly. This may indicate a traffic-related background across the Netherlands originating from distant sources. However, we expect that the origin is not from a distant source but rather due to the diffuse but highly correlated nature of traffic emissions in time. This has been suggested earlier by Schaap and Denier van der Gon (2007), who found a very strong correlation between measured Black Smoke concentrations at rural background stations between different regions in the Netherlands. These authors proved that most of the regional EC concentrations were due to national traffic emissions by using a model.

As for the regional traffic contributions, the industrial (metal) activities/incineration profile has a small spatial variability. Because none of the sites, besides the sites in the Rotterdam area, reflects an industrial area, where these sources may be located, all stations with respect to this source may be regarded as background. This is elaborated by the fact we did not find the highest contribution of this source on either Rotterdam or Schiedam, the only sites with industrial activities in the vicinity. In addition, the profile probably reflects a host of different, diffuse sources, which may explain the low spatial variability.

The factor sea salt also shows a small spatial variability. This was expected as all stations are relatively close to the coast (<100 km), and sea spray aerosols peak at all sites during transport from the sea (Manders et al., 2009). The COD values for crustal material are very similar to those of sea spray. This result is surprising as the sources for mineral dust are many compared to one distinct source for sea salt. Previous work (Mooibroek et al., 2011) postulated that a peak concentration at the same day at all sites during a three day period (23–25 January 2008) of enhanced CRM concentrations may have dominated the COD value. However, removing the episode days from the analysis did not impact the COD value, falsifying this hypothesis. There is no reason to assume this behaviour has changed in this data set.

Finally, the second largest spatial variability is found for the residual oil combustion source. The COD between Schiedam and Rotterdam is the lowest at 0.32, whereas the COD between the sites in the Rotterdam area and the rural sites is almost a factor 2 higher. The higher source contributions as well as the low COD within the Rotterdam area indicate that the source is located in or close to the Rotterdam area. Considering the nearby harbour activities, intensive shipping and petrochemical industries located in the Port of Rotterdam this is quite plausible.

All in all the results are strikingly similar to the results of the separate analysis of $PM_{2.5}$ and PM_{10} (Schaap et al, 2010).

5 Mineral dust contribution in the BOP dataset

5.1 Introduction

In the framework of the Netherlands Research Program on Particulate Matter (BOP programme), an intensive one-year measurement campaign from August 2007 to August 2008 was carried out. During this period PM_{2.5} and PM₁₀ were sampled simultaneously every other day at six locations: Vredepeel, Cabauw and Hellendoorn (rural background stations), Schiedam (urban background) and Rotterdam and Breda (traffic stations). Approximately half of the sampled filters were analysed for PM composition. From these PM composition measurements it was found that the mean contribution of mineral dust to PM₁₀ was 1.6 µg/m³. This contribution was on the low end as compared to nearby countries abroad (Flanders & Germany) and the earlier estimates for the Netherlands as made by Visser et al. (2001). For example, in Flanders over the period 2006-2007 a value of 4.3 µg/m³ is reported (VMM, 2009).

It was proposed to investigate in BOP II the difference in mineral dust contribution in the PM samples between the Netherlands and Flanders by comparing the way in which the PM samples are analysed (XRF versus ICP-MS). However, at the time that the BOP II programme started, the XRF-method as used in Flanders by the VMM was no longer used. Furthermore, the chemical analysis as used in the Netherlands (ICP-MS) has recently also been adapted. Therefore it was decided to investigate another hypothesis which was already suggested during the 1st BOP programme: i.e. the difference in mineral dust concentrations in the Netherlands and Flanders might be explained by the way that the concentrations are calculated from the measured PM elements.

5.2 A comparison of the mean values of the PM components in the Netherlands and Flanders

First, we make a comparison between the components themselves as measured in the Netherlands during the BOP period and the measurements as performed in Flanders during the CHEMKAR period 2006-2007. Table 6 gives an overview for the Netherlands (BOP) and Flanders (VMM, 2009). It is seen that the difference is never larger than a factor of 2.

Table 6

	Al	Si	Fe	Ti	Ca
Rural	0.14	0.36	0.26	0.005	0.25
Urban background	0.25	0.55	0.50	0.010	0.39
Kerbside	0.19	0.51	0.98	0.008	0.40
BOP	0.18	0.44	0.56	0.007	0.33
CHEMKAR	0.16	0.60	0.73	0.005	0.43

5.3 Equations to estimate mineral dust from the PM composition measurements

For the BOP campaign the concentrations of the elements Si and Al are used to estimate the mineral dust (MD) composition in PM₁₀ (Denier van der Gon et al., 2010):

$$\begin{aligned}
 \text{MD} &= 0.49[\text{Si}] + (2.36[\text{Si}] + 2.70[\text{Al}]) \\
 &= 2.85[\text{Si}] + 2.70[\text{Al}]
 \end{aligned}
 \tag{1}$$

Equation (1) was derived by Denier van der Gon et al. (2007, 2008) and is based on the chemical composition of the fine fraction of Dutch top soils, which elements constitute the mineral dust fraction as measured in PM. Notice that equation (1) is expressed in terms of Al and Si only, but it implicitly takes into account the other soil minerals which contribute to mineral dust in PM (for details see Denier van der Gon et al., 2010).

More soil elements are used in the mineral dust equation as used by Flanders to estimate the mineral dust contribution in PM. Next to Al and Si, Ca, Fe and Ti are explicitly used to estimate the mineral dust concentration in PM:

$$\text{MD} = 2.2[\text{Al}] + 2.49[\text{Si}] + 1.63[\text{Ca}] + 2.42[\text{Fe}] + 1.94[\text{Ti}]. \quad (2)$$

The above equation is based on an evaluation of the equation of soil as derived in the late 1980's based on data from the Western Fine Particle Network and from the soil composition table from F.J. Pettijohn, *Sedimentary Rocks*, (NY, Harper & Row, 1949, 1957, and 1975).

In this report the BOP dataset is used to calculate mineral dust concentrations using the two equations as mentioned above and to make a comparison between these two different ways of calculating mineral dust concentrations. For these calculations, the concentrations of all components have been taken from the BOP dataset taking into account the recovery factor of the experiment. These factors are given in Schaap et al. (2010) and are respectively: 70% for Al, 50% for Si, 90% for Ca, 70% for Ti and 80% for Fe.

5.4 A comparison of mineral dust calculations

Figure 14 (upper panel) shows a scatter plot of the mineral dust contribution in PM₁₀ from the equation as used for the BOP analysis (equation (1) (on the x-axis)) and the equation as used in Flanders (equation (2) (on the y-axis)). An orthonormal regression analysis yields a regression coefficient of 1.58 ± 0.05 . A total number of 558 points was used for this analysis for which the mean value according to the BOP analysis (equation (1)) yields $1.7 \mu\text{g}/\text{m}^3$, whereas the equation used for the VMM analysis (equation (2)) yields a value of $3.4 \mu\text{g}/\text{m}^3$. Notice that this is a factor of 2 instead of 1.6. Repeating the analysis, this time leaving out the four points with values higher than $10 \mu\text{g}/\text{m}^3$ on the x-axis yields a regression coefficient of 2.03 ± 0.06 . This scatter plot is shown in Figure 14 (bottom panel) and is in line with the ratio of the mean concentrations as mentioned above.

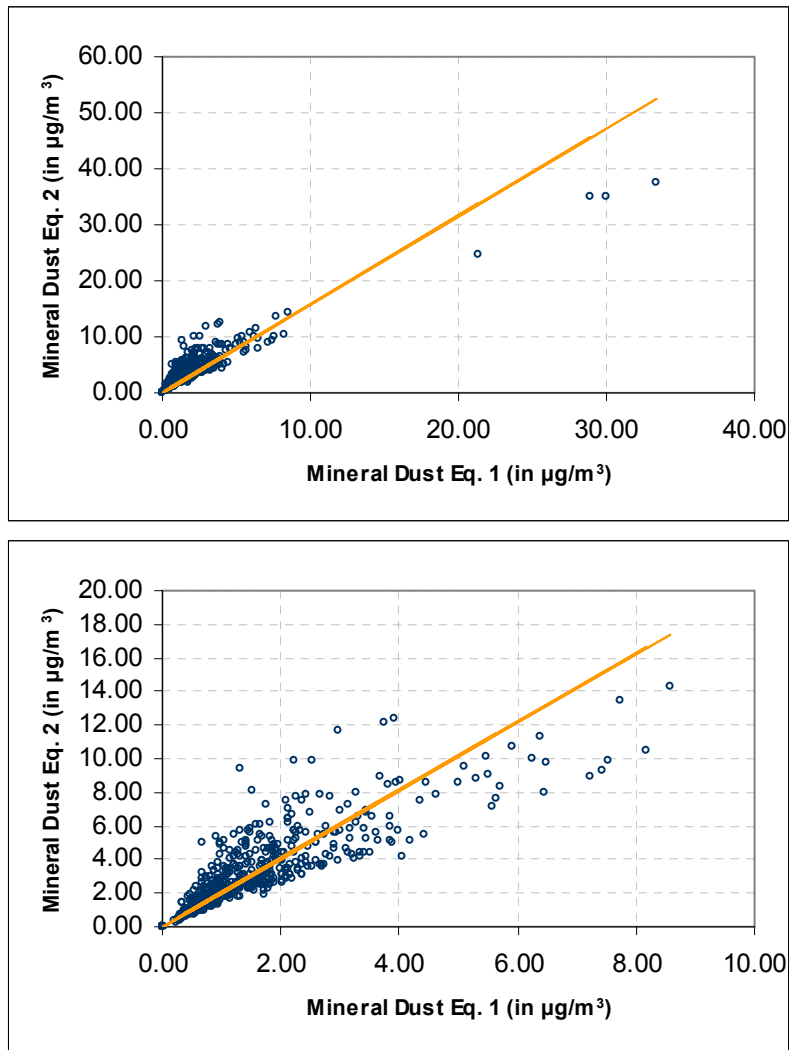


Figure 14 Scatter plot of the mineral dust concentrations as calculated for the BOP analysis (x-axis) and for the concentrations as calculated in Flanders (y-axis). The top panel shows all data, whereas the lower panel only shows data for concentration values lower than $10 \mu\text{g}/\text{m}^3$ on the x-axis.

5.5

A comparison of mineral dust calculations focusing on Si and Al

Additionally we compare equation (1) with equation (2) in which for the last equation only the contributions from Al and Si components are calculated. This obviously yields a regression line with a correlation coefficient R^2 of unity: the regression coefficient equals 0.86. Next, a regression analysis is performed for the equation as used for the BOP analysis (equation (1) (on the x-axis)) and the equation as used in Flanders minus the Si and Al contribution (on the y-axis). Figure 15 shows the result. The regression coefficient equals 1.23 ± 0.06 .

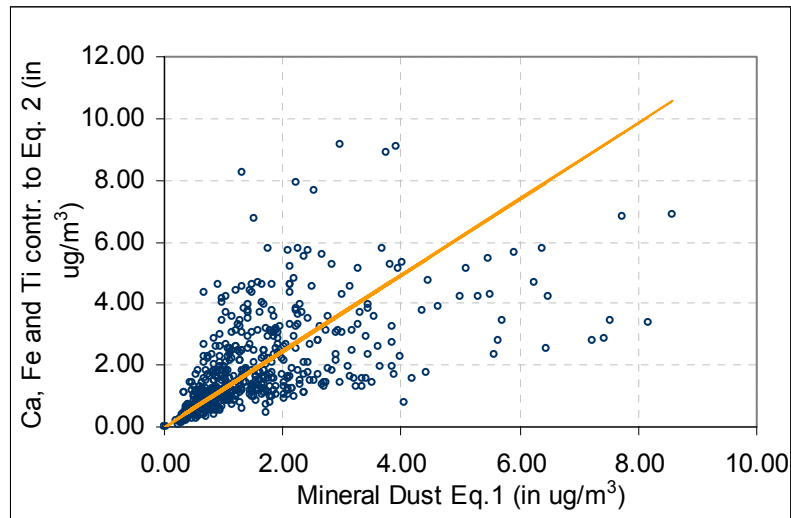


Figure 15 Scatter plot of the mineral dust concentrations as calculated for the BOP analysis (x-axis) and for the Ca, Fe and Ti contribution to the concentrations as calculated in Flanders (y-axis)

Repeating this analysis but now splitting up the regression analysis in rural, urban background and curbside locations we get the following regression coefficients:

	Eq 1 vs Eq 2	Eq 1 vs Eq 2	Eq 1 vs Eq 2
	Al & Si	Al, Si & Ca	Al, Si, Ca, Fe, (Ti)
Rural	0.86	1.10	1.50
Urban Background	0.85	1.14	1.75
Traffic	0.86	1.20	2.50

One can see that the contribution of Ca, Fe and Ti to the total mineral dust concentration as calculated in equation (2) increases in going from rural to urban background to traffic locations. This is in line with the fact that Ca and Fe are most likely related with traffic and construction activities. These are to a lesser extend present in rural background locations. This can be seen in Figure 16 which shows the relative contribution to the sum of the five elements Al, Si, Ca, Fe and Ti for a rural location (Cabauw) and a traffic location (Breda).

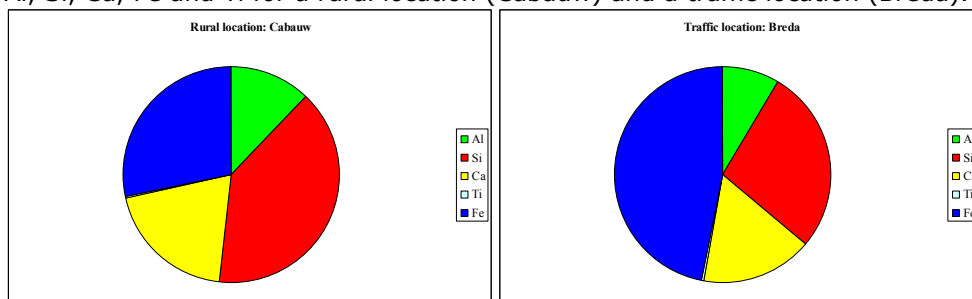


Figure 16 Relative contribution of the five elements Al, Si, Ca, Fe and Ti which are used in the mineral dust equations. The left panel is an example of a rural background location, the right panel is an example for a traffic location.

It is concluded from the analysis above that the equations (1) and (2) are describing different parts of mineral dust: equation (1) is especially focused on determining the wind-blown dust from the top soil, whereas equation (2)

includes components (Fe & Ti), which are related with resuspended road dust. These additional components are contributing significantly to the mineral dust concentrations at traffic locations.

6 Conclusions

6.1 PMF analysis

The results of the EPA-PMF analysis on the combined PM_{2.5} and PM₁₀ data sets showed similar results compared to the separate analysis of each fraction. The same source types were identified, although a clear distinction between nitrate and sulphate-rich secondary aerosol was not found in this study. Overall, the result from this study confirms the validity of the results found in the separate PM_{2.5} and PM₁₀ studies (Schaap et al., 2010). This indicates that the EPA-PMF method for source apportionment is a very robust method.

By combining the data sets into one dataset, some details are lost in the analysis as compared to the separate EPA-PMF analyses. An example of the loss of details can be seen in the correlation between the summed mass (based upon measured species) and measured mass. The found mass closure for the combined data set is not as convincingly as found in the separate studies.

This research has however also shown that most of the EC mass is still contributed to a different source factor for PM_{2.5} than for PM₁₀. Since the EPA-PMF method was shown to be very robust, this implies that the difference is implicitly present in the dataset. The cause of the inconsistencies in the dataset remains unclear, although a number of options have been excluded.

6.2 Mineral dust

The results from section 5 show that the mineral dust contribution to PM depends strongly on the equation which is used to calculate this contribution. Earlier results reported in BOP mentioned that the mineral dust contribution was lower in the Netherlands as compared to the values found by the VMM in Flanders. The results from section 5 show that a difference of the order of 2 can be completely attributed to the way in which the mineral dust contribution is calculated from the measured components in PM.

In section 5 it was shown that the MD contribution from Al and Si as calculated in the Netherlands and Flanders differ by a factor of 0.86. Subsequently it was shown that the additional elements which are used in Flanders, i.e. Ti, Ca and Fe, are making a strong contribution to the MD component at street locations.

Finally it was shown that the concentrations of the components Si, Al, Fe, Ca and Ti as measured in the BOP and Chemkar campaign are not strongly deviating, and certainly less than a factor of 2.

Taking the above into account one can conclude that the difference in MD contribution in PM as measured in the Netherlands and Flanders is not as big as was previously claimed: the differences are below the previously claimed factor of 2. The strongest difference is caused by the way in which the MD contribution to PM is calculated: Flanders includes the components Fe, Ca and Ti, which are especially contributing in areas with traffic and construction activities.

Overall, it is concluded from this analysis that the equations (1) and (2) in section 5 are describing different parts of mineral dust: equation (1) is especially focused on determining the wind-blown dust from the top soil, whereas

equation (2) includes components (Fe & Ti), which are related with resuspended road dust. These additional components are contributing significantly to the mineral dust concentrations at traffic locations.

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A Methodology

A.1 EPA Positive Matrix Factorization (ME-2)

The general receptor modelling problem consists of the following objectives: determine (i) the number of aerosol sources, p , (ii) the chemical composition profile of each source, and (iii) the amount that each of the p sources contributes to the measured concentration. This problem can be solved by decomposing a matrix of speciated sample data.

To decompose the speciated sample matrix X , defined as an i -by- j data matrix consisting of the measurements of j chemical species in i samples, we use a multivariate factor analysis tool called Positive Matrix Factorization (PMF). The objective of PMF is to determine the number of factors, p , the species profile f of each factor and the amount that each of the p factors contributes g to each sample (see equation A.1):

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (\text{A.1})$$

where e_{ij} is the residual for each sample/species as defined by equation A.2:

$$e_{ij} = x_{ij} - \sum_{k=1}^p g_{ik} f_{kj} \quad (\text{A.2})$$

$(i = 1, \dots, n; j = 1, \dots, m; k = 1, \dots, p).$

Additionally, a non-negativity constraint is applied, forcing the source contributions to contain either positive or small negative values. PMF is based upon a weighted least squares fit where the known standard deviations for the analysis in matrix X are used to determine the weights of the residual elements e_{ij} . This allows adjustment of the influence of each data point, depending on the confidence of the individual measurement. As in other applications using least squares fit, PMF tries to minimize the sum-of-squares (Q) expression:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right)^2 \quad (\text{A.3})$$

in which the values u_{ij} represent the user-defined error estimates for the values x_{ij} .

Depending on the initial starting point, multiple solutions (local minima) may be found in some cases. This is one of the disadvantages of a least squares approach. Therefore, it is advisable to perform various runs from different random starting points to ensure that the same solution is obtained. In the case of several local minima, Sirkka and Paatero (1994) suggest keeping the solutions with the lowest $Q(E)$ -value.

The first program to solve the PMF problem described above was introduced by Paatero and Tapper (1994) and was called Positive Matrix Factorization (PMF). Further development has led to the PMF2 version in 2000 (Paatero, 2000), which has been used in numerous publications dealing with source apportionment. Subsequently Paatero started development on a more flexible program, known as the multilinear engine, in the late nineties. Currently this program is in its second version and is referred to as ME-2. The ME-2 program is, despite the name, the underlying program used to solve the PMF problem in the program EPA-PMF (EPA PMF Users guide). EPA PMF provides a user interface to feed the data and user specifications to ME-2. The output of ME-2 is formatted in the EPA-PMF program, making it easier for the user to interpret the results.

Comparison between both PMF and ME-2 showed similar results, with ME-2 providing a better source separation (Kim et al., 2007, Norris et al., 2008). In this study we used the PMF version EPA-PMF 3.0, developed by NERL-US.EPA (Research Triangle Park, North Carolina, USA, 2008). All calculations were performed in robust mode, thus limiting outliers to influence the final solution.

A.2 Inclusion of species

Not every chemical species in the speciated sample matrix X may provide valuable information to solve the PMF problem. In fact, Paatero and Hopke (2003) found including all species in factor analytical models may actually degrade the solution. In this study Paatero and Hopke suggest using the signal-to-noise ratio (S/N) for each species as an indicator to qualify species either as strong enough to be included in the model; bad enough to be severely down-weighted, if not removed; or weak (between strong and bad), but retainable in the model and slightly down-weighted. The signal-to-noise ratio in EPA PMF v3.0 is calculated as:

$$\left(\frac{S}{N}\right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - s_{ij})^2}{\sum_{i=1}^n s_{ij}^2}} \quad (\text{A.4})$$

Paatero and Hopke also provided guidelines to use the signal-to-noise ratio: a species is categorized as 'bad' if the signal-to-noise ratio is less than 0.2 and is categorized as 'weak' if the signal-to-noise ratio is greater than 0.2 but less than 2. Subsequently, species with a signal-to-noise ratio greater than 2 are categorized as 'strong'. Other than using the signal-to-noise ratio it is important to consider other information that is available, e.g. is the species chemically distinct, how many samples are missing or below the detection limit.

Categorizing a species as 'bad' will exclude the species from the analysis, whereas the categorization of 'weak' will lead to an increase of the uncertainties by a factor of three.

A.3 Number of factors

The determination of the number of factors has been a much debated issue in the application of the PMF problem. Selecting the number of factors that will provide the best description of the dataset is always a compromise: too few factors will likely combine sources in one source profile, whereas too many factors will dissociate a real factor into additional but non-existing sources.

A well-known indicator for selecting the number of factors is the goodness-of-fit value $Q(E)$ (equation 3). If the dimensions and all estimates for the standard deviation are correct, the $Q(E)$ -values should be distributed according to a χ^2 (chi²) distribution (Paatero and Tapper, 1993; Chueinta et al., 2000). Song et al. (2001) suggested using $Q(E)$ for selecting the number of factors, provided reasonable estimates for the standard deviation are available, by comparing the calculated $Q(E)$ with an expected value of $Q(E)$.

The expected value of $Q(E)$ is approximately equal to the number of data values minus the number of essential free parameters fitted to the data. This value is often called the degrees of freedom. (Paatero et al., 2002b):

$$E(Q) = ij - p(i + j) \quad (\text{A.5})$$

However, despite using the 'robust' mode in which outliers have less influence on the calculated $Q(E)$ value, it still might be difficult to assess if the calculated $Q(E)$ is as expected or too large. In this case it might be more helpful to examine the scaled residuals.

In a well-fit model the ratio between the residuals e_{ij} and the error estimates s_{ij} (e.g. e_{ij}/s_{ij}) should be symmetrically distributed and fluctuate between a range of -3 and $+3$, but preferably less. If the scaled residuals for each species are between -3 and $+3$, then the estimate for the standard deviation of this species is acceptable. However, if the scaled residuals are too large, then either the estimate for the standard deviation being used is too small or the number of factors has to be re-evaluated. The re-evaluation of factors should also be performed in the case of skewed residuals.

Various other suggestions for the selection of the number of factors are available. For example, Lee et al. (1999) proposed the use of the scaled residual matrix (R) to determine the number of factors. For each specific number of factors, two indicators to identify the species having the least fit and the most imprecise fit are obtained from R : IM , the maximum individual column mean, and IS , the maximum individual column standard deviation. When the number of factors is increased to a critical value, both IM and IS drop significantly and the optimal number of factors can be determined. If the drop is not sharp, a range of number of factors must be evaluated by processing the data and examining the resulting profiles and the temporal variation of the individual contributions.

The approaches described here for determining the number of factors can be helpful; however, there is no definitive indicator to determine the number of factors needed. In general, it still comes down to a judgment call made by the data analyst on whether or not the derived factors look reasonable.

A.4 Rotational freedom

Even though there will be a global minimum in the least squares fitting process, there may not be a unique solution because of the rotational ambiguity. The addition of constraints can reduce the rotational freedom in the model, but non-negativity alone does not generally produce a unique solution (Paatero et al., 2002b). The rotational (e.g. linear transformation) problem can be illustrated, in matrix notation, by:

$$X = GF + E = \bar{G}\bar{F} + E \quad (\text{A.6})$$

Both solutions in equation A.6 will produce the same Q value and, therefore, it can be said that the first solution can be rotated so that it becomes equal to the second solution. Based on the properties of an identity matrix I , the following is true:

$$X = GF = GTF = G(TT^{-1})F \quad (\text{A.7})$$

in which both T and T^{-1} are each one of the potential infinitive number of possible transformation matrixes.

With the help of the matrix T and the inverse T^{-1} matrix, a transformation can be defined by:

$$\bar{G} = GT \text{ and } \bar{F} = T^{-1}F \quad (\text{A.8})$$

The transformation defined by equation A.8 is considered to be a rotation. However, this rotation is only allowed when all elements in both G and F are non-negative and, in some cases, this condition will limit the rotations in such way that a unique solution may be found (Paatero et al., 2002b).

To provide the user with some control over the rotations, the PMF algorithm provides a 'peaking parameter' called 'FPEAK'. If a value of zero is used for this parameter, PMF will produce a more 'central' solution. The use of nonzero values allows sharper peaks to be obtained, which are to be expected in source profiles, and will limit the rotational freedom (Paatero, 2000; Hopke, 2003).

A.5 Compare calculated contributions with measured mass

The results of the EPA-PMF analysis will reproduce the data and ensure, among other things, that both the source profiles as the source contributions are non-negative. However, it has not taken in account the total mass. The easiest way to estimate the total mass contributions is by calculating the sum of the species contributions. By using this method the assumption is made that the total mass is fully represented by the species, also known as mass closure. However, mass closure is rarely achieved. Even with the analysis of important aerosols components, a fraction of the PM mass remains unidentified (Almeida et al. 2006). Part of this issue can be resolved by assuming all measured metals are present as oxides and multiplying these metals with a factor to account for the oxides (e.g. [1.89*aluminium], [2.14*silicon] (Solomon et al., 1989)). For the components generally found in crustal material the assumption above will hold, however it remains to be seen if the elemental compositions of other sources indeed contain metals as oxides.

To solve the problem two well established methods exists. One of these methods is using multi linear regression to establish scaling constants which can be used to calculate the source contributions. However, this method uses the assumption that the species which were not measured are strongly correlated to the measured species or that they represent sources that add negligible mass to the particulate matter samples. If this assumption is true then the sum of the source contributions g_{ik} should be approximately equal to the measured total mass (Juntto and Paatero, 1994; Hopke, 2003).

In the original formula on which PMF is based a multiplicative scaling factor can be added as shown in equation A.9.

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} = \sum_{k=1}^p g_{ik} \frac{s_k}{s_k} f_{kj} + e_{ij} \quad (\text{A.9})$$

In this formula s_k represent the scaling constants. These scaling constants can be calculated by performing a regression of the measured mass against the source contributions located in the G -matrix. Each of the s_k values must be non-negative. Negative values are considered to be an indication of an overestimation of the number of factors chosen by the analyst.

Since the scaling constants s_k are now known, the predicted total mass for each day (defined as the sum of all sources) m_i can be determined by:

$$m_i = \sum_{k=1}^p s_k g_{ik} \quad (\text{A.10})$$

The second method uses the inclusion of the total measured mass as an independent variable in the EPA-PMF modelling, effectively forcing the model to apportion the total mass for each profile as part of the solution. Because this total variable should not have a large influence on the solution it is given a high uncertainty by categorizing it as a weak variable. (Norris et al., 2008) The quantitative source contributions on each day can be obtained by using the apportioned mass for each source as the scaling constants s_k in equation A.10, leading to the predicted total mass for each day m_i .

A.6 Conditional probability function (CPF)

Kim and Hopke (2004) demonstrated the usefulness of a new technique by using the Conditional Probability Function (CPF) in which sources are likely to be located in the directions that have high conditional probability values (Hwang and Hopke, 2006; Xie and Berkowitz, 2006). The CPF was calculated using the source contributions (G) from the PMF analysis and the wind direction values measured on a meteorological station nearby. To match the hourly wind data, each daily contribution was assigned to each hour of a given day (Kim et al., 2003).

The CPF is defined as:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (\text{A.11})$$

where $m_{\Delta\theta}$ is the number of occurrence from wind sector $\Delta\theta$ that exceed the threshold criterion, and $n_{\Delta\theta}$ is the total number of data from the same wind sector. In this study $\Delta\theta$ was set at 30° , and calm winds (< 1 m/s) were excluded. The threshold was set at the upper 25th percentile of the contribution from each source.

Wind data were obtained from the Royal Netherlands Meteorological Institute (KNMI) which operates the meteorological stations in The Netherlands. The data from the meteorological site located nearest to the receptor site were used to calculate the CPF.

A.7 HYSPLIT

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model can be used to calculate air mass back-trajectories during a specific period. By performing a backwards trajectory the model follows a single air parcel backwards in time, providing information about the origin of a local or regional source.

Research by Gebhart et al. (2005) showed trajectories starting higher above the surface tend to be faster and may identify sources farther away than those started at lower heights. When trying to identify the source of secondary aerosol, either sulphate-rich, or nitrate-rich, a mixture of higher starting heights and a longer timeframe must be used.

In case of expected contribution of Saharan dust, which frequently rains out, it is wise to examine starting heights ranging at least from 0 – 1,000 m above the receptor point, during a longer timeframe. When local sources are observed, calculations should be performed somewhere between 0 – 50m above the receptor point with a small timeframe. Generally speaking the concentrations in this study have been typically measured at approximately 2-3 m above ground level.

Whenever possible the default settings were applied, vertical motion was used in the default mode and meteorological data from GDAS (2005 – present) was used.

A.8 Coefficients of divergence (COD)

The spatial variability or the degree of uniformity of the calculated source contributions at the selected sites was determined using the coefficients of divergence (COD) (Kim et al., 2005, Kim and Hopke, 2005 and Kim and Hopke, 2008). The COD is a coefficient used to determine the resemblance between objects or the variables describing these objects. For the spatial distribution the COD approaches zero if the source contributions at the compared sites are highly correlated. In case the source contributions are very different the COD approaches unity. We have excluded (small) negative daily source contributions from the calculation.

B Data pre-processing

B.1 Multiple imputation for missing data

As mentioned earlier positive matrix factorization (PMF) is designed to deal with a 'complete-case' data set (for all samples data are available for all measured parameters), a condition rarely met in environmental surveys. In this study we have a data set with missing values for EC/OC/SIA/CI.

By using the average and standard deviations from the log-transformed data we randomly drew new data from the normal distribution and recalculated the average and standard deviations of the new data set including the imputed data. This process is repeated 2,500 times. To obtain a full reflection of uncertainty, the entire process is simultaneously performed on three data sets, each using rather extreme different starting values as estimates for the missing values. The standard deviation between the four replicates is used as an uncertainty estimate for each sample. Approximately one third of the samples for the species EC/OC/SIA/CI was missing. Using the MI technique we were able to provide estimates for these unknown concentrations.

We have found that three samples for the PM₁₀ data contained very low (near zero) concentrations for EC/OC/SIA/CI. Since these samples can distort the imputation process we have eliminated these samples.

Rotterdam:	14-10-2007: EC/OC/SIA/CI
Rotterdam:	12-12-2007: EC/OC/SIA/CI
Hellendoorn:	02-06-2008: SIA/CI

B.2 Correlations between measured and imputed data

A strong correlation between the species measured in both the $PM_{2.5}$ and PM_{10} fraction has to exist for those species primarily contributed by the $PM_{2.5}$ fraction. We compared the correlations between the actual measured data and the measured data including imputed values of both fractions (hence, we compared the correlations between $PM_{2.5}$ and PM_{10} for measured only and for measured including imputed). This approach gives us an idea of the effect of imputation on the underlying correlations. As input for the complete data set we used the data set containing values below the MDL replaced with half the MDL and the imputed values (see also section 2.4). For the measured data the imputed values were replaced by NaN values in the complete data set.

Since we did not have missing data for the ICP-MS set, the results of the comparison between the Pairwise Pearson's correlation coefficients has to be small. The maximum allowed absolute difference between the correlation coefficients of the complete and measured data set was set to 0.001. We flagged species with a difference larger than the maximum allowed absolute difference. For the ICP-MS values there were no differences found, however the EC/OC/SIA/Cl correlation coefficients had changed.

Using plots containing both the measured and imputed data we were able to determine the influence of the imputed data. We have found the correlations between the same specie in both $PM_{2.5}$ and PM_{10} changed only moderately.

Table 6 Overview of the correlations between $PM_{2.5}$ and PM_{10} measurements for several species for both the complete (measured + imputed) data set and for measured data only

Species	Measured data set	Complete data set
OC	0.7256	0.5952
EC	0.9406	0.8828
NH ₄	0.9200	0.9198
NO ₃	0.9157	0.8923
SO ₄	0.9389	0.8708
Cl	0.6964	0.6859

Compared to the other species OC shows a larger decrease in correlation coefficient. The plots of measured and imputed data for OC show a high degree of randomness between both fractions for both the measured and imputed values.

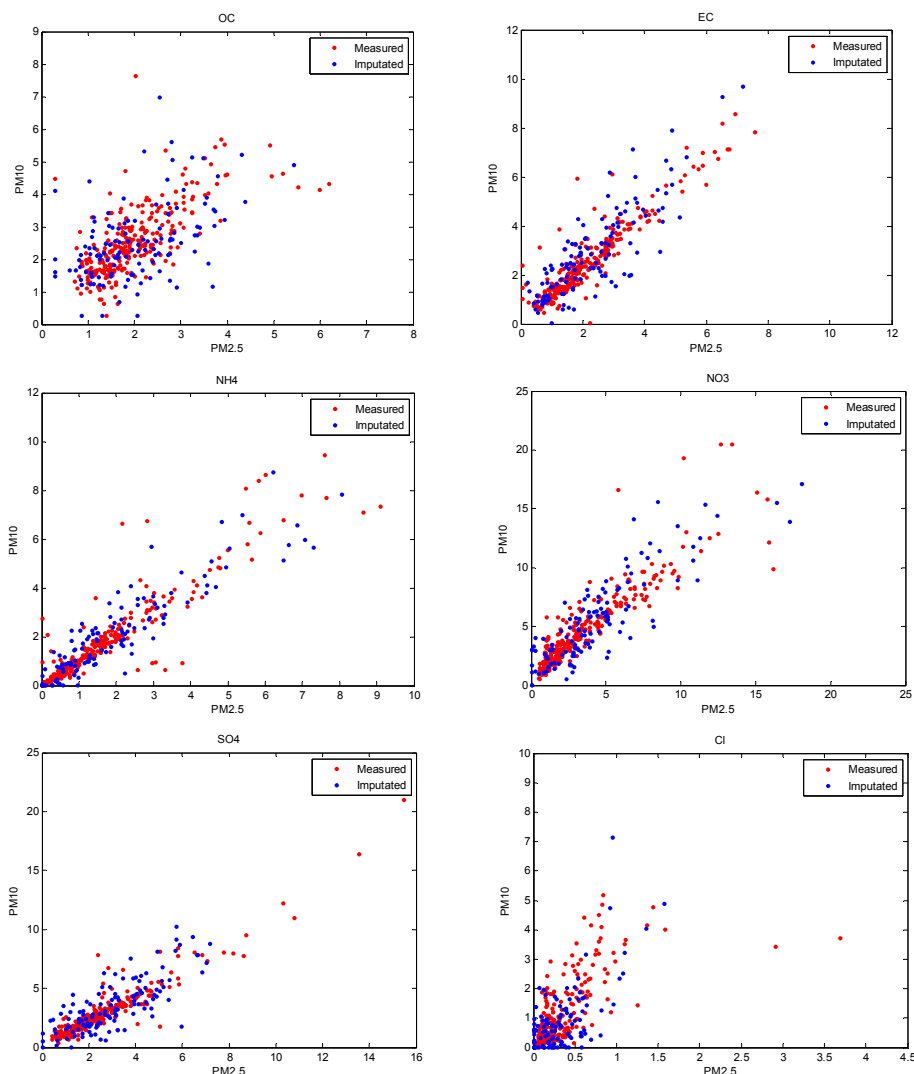


Figure 16 The influence of measured vs imputed values for EC/OC/SIA/Cl
The blue dots are the imputed values, whereas the red dots denote the measured values. In all cases it can be seen that the imputed values respect the variability of the measured values in $PM_{2.5}$ and PM_{10} . There are some species (e.g. OC, Cl) which show a larger variability between the $PM_{2.5}$ and PM_{10} measurements.

B.3 Dealing with measurements below the limit of detection

Detailed information about the uncertainties and MDL for the ICP-MS analysis is available and is described in detail elsewhere (Schaap et al., 2011). For both the results of the ICPMS and SIA analysis uncertainties for each measurement were given. For the ICPMS detailed information was available on the minimum detection limit (MDL). The MDL for the NH_4 /EC/OC analysis were not given. Based upon expert judgment the MDL for OC was set at half the measured averaged blank concentration ($0.6 \mu g/m^3$), the MDL of EC was set to 1/6 of the OC MSL ($0.1 \mu g/m^3$) and the NH_4 MDL was set to $1 ng/m^3$. Other information about the uncertainties for the SIA analysis can be found in Schaap et al. (2011).

Initially the dataset contained reported values for the data below the minimum detection limit (MDL). In our dataset some of these reported data are negative concentrations. Due to the large measurement error of values below the MDL negative concentrations are plausible. In factor analysis these measurements should be given a high uncertainty in order to provide a low weight in finding the solution.

For the species Beryllium, Lithium and Yttrium more than 90% of all available samples were below the limit of detection on both PM data sets. Due to the non-existing variability in these components we have removed them from the final analysis. Species with less than 50% of the data available and above the MDL may not contain concentrations with sufficient variability to be useful. Provided the signal to noise ratio (see Appendix A.3) is reasonable these species may be included. (Brown et al., 2005).

A general approach for handling data below the MDL was given by Pollisar et al. (1998) and consists of replacing the data below the MDL with half the MDL. The corresponding uncertainty for these values was set to 5/6 times the MDL. The EPA-PMF fundamentals and user's guide uses the same approach for calculating the uncertainties when an equation-based uncertainty file is used (Norris et al., 2008). However, the concentration file, used as input for EPA-PMF, is not modified by EPA-PMF for data below the MDL.

For the sake of continuity, simplicity and comparison between other studies (Kim et al., 2003; Kim and Hopke, 2004; Nicolás et al., 2008) we have used the proposed method by Polissar (1998). Concentrations below the MDL were replaced by half the MDL and the corresponding uncertainties were set to $5/6 \times \text{MDL}$.

We first replace the given uncertainties for measurements below the MDL with 5/6 of the MDL. The second step is setting the uncertainties of all imputed values to four times the imputed value. Doing the MDL replacement first ensures that imputed values below the MDL are correctly weighted with (in general) a higher uncertainty than 5/6 times the MDL.

B.4 Using samples that didn't pass the QA-check

There are two subsets of rules defined, one detailing the condition of the weighing room and one detailing both unreliable measurements (e.g. fallen filters) and mechanical errors (e.g. failed pumps). In case of severe mechanical errors no additional measurements could be performed. However, in most cases the rejected samples still contain useful information, albeit with a higher uncertainty.

Positive matrix factorization (EPA-PMF) uses the uncertainty matrix to apply weights for each separate measurement. This allows us to include certain samples which might not meet the initial strict requirements, but might still contain useful information.

We therefore multiplied the associated uncertainty of that sample by a factor 2 when the total mass measurement was rejected due to the rules associated with the condition of the weighing room. In case of unreliable measurements or

measurements with mechanical errors we applied a factor 4 to the associated uncertainty.

Individual species can also have a validation code; rejected samples will have their uncertainties multiplied by a factor 4 whereas samples that were not validated will have their uncertainties multiplied by a factor 2.

C Species overview

Table 7 Overview of classification (weak and strong) in EPA-PMF 3.0 for each species, as well as some statistics (signal to noise ratio, minimum, 25th and 75th percentile, median and maximum) calculated by EPA-PMF 3.0

Fraction	Species	Classification	S/N	Min	P25	Median	P75	Max
PM _{2.5}	TM	Weak	14.488	0.500	10.564	15.187	23.516	71.158
PM _{2.5}	Al	Strong	7.333	0.001	0.016	0.023	0.038	0.959
PM _{2.5}	As	Strong	3.882	0.000	0.000	0.001	0.001	0.004
PM _{2.5}	Ba	Strong	2.559	0.001	0.003	0.004	0.006	0.514
PM _{2.5}	Ca	Weak	0.165	0.036	0.036	0.036	0.100	0.906
PM _{2.5}	Cd	Weak	1.219	0.000	0.000	0.000	0.000	0.002
PM _{2.5}	Co	Weak	1.106	0.000	0.000	0.000	0.000	0.001
PM _{2.5}	Cr	Strong	3.347	0.000	0.002	0.003	0.003	0.019
PM _{2.5}	Cu	Strong	6.671	0.000	0.002	0.003	0.006	0.091
PM _{2.5}	Fe	Strong	4.140	0.014	0.045	0.083	0.165	0.709
PM _{2.5}	K	Weak	0.492	0.018	0.047	0.069	0.109	4.841
PM _{2.5}	Mg	Strong	4.028	0.014	0.028	0.041	0.057	0.732
PM _{2.5}	Mn	Strong	5.161	0.000	0.002	0.003	0.005	0.027
PM _{2.5}	Mo	Strong	3.551	0.000	0.000	0.001	0.001	0.011
PM _{2.5}	Na	Strong	3.289	0.027	0.086	0.161	0.305	1.770
PM _{2.5}	Ni	Strong	4.872	0.000	0.001	0.002	0.004	0.021
PM _{2.5}	P	Weak	0.297	0.032	0.032	0.091	0.110	0.172
PM _{2.5}	Pb	Strong	2.979	0.001	0.003	0.006	0.011	0.116
PM _{2.5}	Sb	Strong	5.926	0.000	0.000	0.001	0.001	0.006
PM _{2.5}	Se	Strong	2.736	0.000	0.000	0.001	0.002	0.042
PM _{2.5}	Si	Weak	0.286	0.023	0.047	0.064	0.090	1.515
PM _{2.5}	Sn	Strong	5.122	0.000	0.001	0.001	0.002	0.088
PM _{2.5}	Sr	Strong	3.759	0.000	0.001	0.001	0.001	0.113
PM _{2.5}	Ti	Strong	5.629	0.000	0.001	0.001	0.002	0.024
PM _{2.5}	V	Strong	7.327	0.000	0.001	0.002	0.007	0.037
PM _{2.5}	Zn	Strong	3.165	0.004	0.078	0.095	0.111	0.331
PM _{2.5}	OC	Weak	0.759	0.280	1.399	1.874	2.560	7.408
PM _{2.5}	EC	Weak	0.758	0.044	1.251	1.920	2.948	11.640
PM _{2.5}	NH ₄	Weak	0.800	0.003	0.551	1.245	2.256	9.088
PM _{2.5}	NO ₃	Weak	0.809	0.011	1.474	2.811	5.099	20.943
PM _{2.5}	SO ₄	Weak	0.813	0.015	1.539	2.382	3.506	15.472
PM _{2.5}	Cl	Weak	0.801	0.007	0.101	0.225	0.461	4.266
PM ₁₀	TM	Weak	19.802	0.500	16.698	23.170	33.122	86.214
PM ₁₀	Al	Strong	7.333	0.001	0.041	0.077	0.135	2.516
PM ₁₀	As	Strong	4.419	0.000	0.000	0.001	0.001	0.004
PM ₁₀	Ba	Strong	2.568	0.001	0.005	0.007	0.012	0.570
PM ₁₀	Ca	Weak	0.034	0.036	0.158	0.243	0.349	1.691
PM ₁₀	Cd	Weak	1.420	0.000	0.000	0.000	0.000	0.002
PM ₁₀	Co	Weak	1.639	0.000	0.000	0.000	0.000	0.001
PM ₁₀	Cr	Strong	3.348	0.000	0.003	0.004	0.006	0.034
PM ₁₀	Cu	Strong	6.692	0.000	0.004	0.007	0.024	0.139
PM ₁₀	Fe	Strong	4.262	0.014	0.141	0.255	0.601	2.654
PM ₁₀	K	Weak	0.493	0.018	0.096	0.136	0.181	5.559
PM ₁₀	Mg	Strong	5.632	0.014	0.077	0.121	0.187	0.913

Fraction	Species	Classification	S/N	Min	P25	Median	P75	Max
PM ₁₀	Mn	Strong	5.248	0.000	0.004	0.007	0.013	0.138
PM ₁₀	Mo	Strong	5.493	0.000	0.001	0.001	0.002	0.010
PM ₁₀	Na	Strong	3.347	0.027	0.249	0.616	1.187	5.543
PM ₁₀	Ni	Strong	4.880	0.000	0.002	0.003	0.005	0.021
PM ₁₀	P	Weak	0.296	0.032	0.032	0.097	0.122	0.194
PM ₁₀	Pb	Strong	2.988	0.001	0.005	0.008	0.014	0.101
PM ₁₀	Sb	Strong	6.135	0.000	0.001	0.001	0.003	0.017
PM ₁₀	Se	Strong	2.881	0.000	0.000	0.001	0.002	0.038
PM ₁₀	Si	Weak	0.282	0.023	0.095	0.153	0.249	4.146
PM ₁₀	Sn	Strong	5.224	0.000	0.001	0.002	0.005	0.092
PM ₁₀	Sr	Strong	3.762	0.000	0.001	0.002	0.002	0.122
PM ₁₀	Ti	Strong	5.666	0.000	0.002	0.004	0.006	0.066
PM ₁₀	V	Strong	7.333	0.000	0.002	0.003	0.008	0.038
PM ₁₀	Zn	Strong	3.166	0.004	0.080	0.101	0.119	0.369
PM ₁₀	OC	Weak	0.758	0.280	1.802	2.443	3.203	8.592
PM ₁₀	EC	Weak	0.757	0.044	1.534	2.399	3.588	11.574
PM ₁₀	NH ₄	Weak	0.814	0.003	0.608	1.327	2.401	10.840
PM ₁₀	NO ₃	Weak	0.815	0.011	2.549	4.002	6.909	22.351
PM ₁₀	SO ₄	Weak	0.816	0.015	1.770	2.748	3.970	21.024
PM ₁₀	Cl	Weak	0.827	0.007	0.238	0.605	1.493	9.021

D Rotterdam

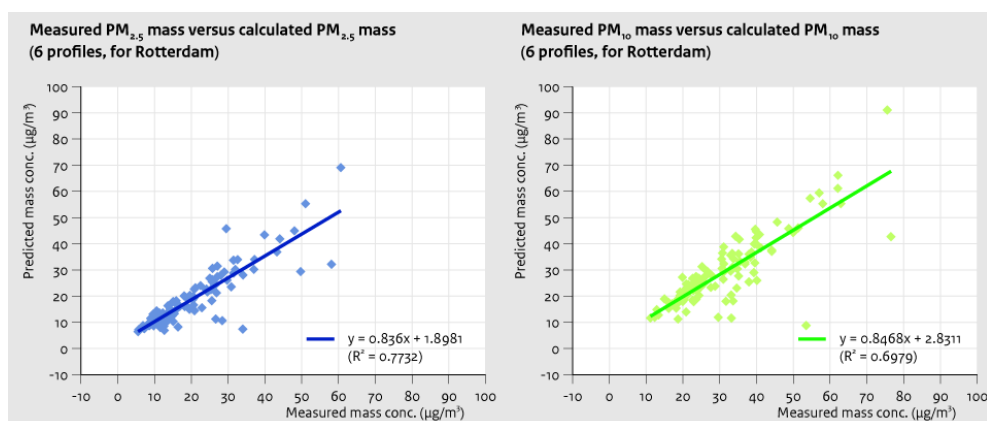


Figure 17 Comparison of measured mass and apportioned mass at Rotterdam for both PM_{2.5} (left, in blue) and PM₁₀ (right, in green) data sets, based on the contributions of all six factors
 The solid lines are the linear regression results.

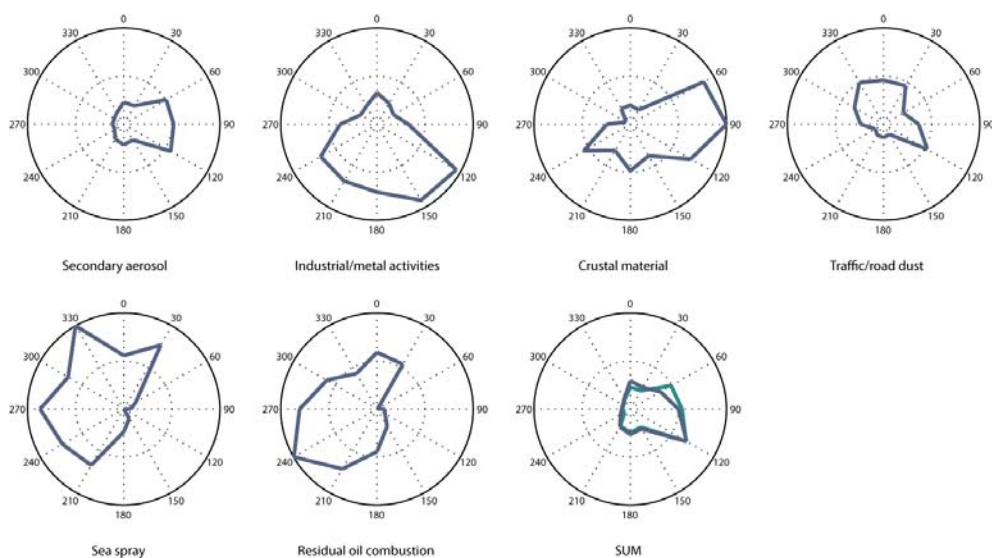


Figure 18 CPF plots for the six source profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport
 The blue line represents the results for PM_{2.5} and the green line for PM₁₀.

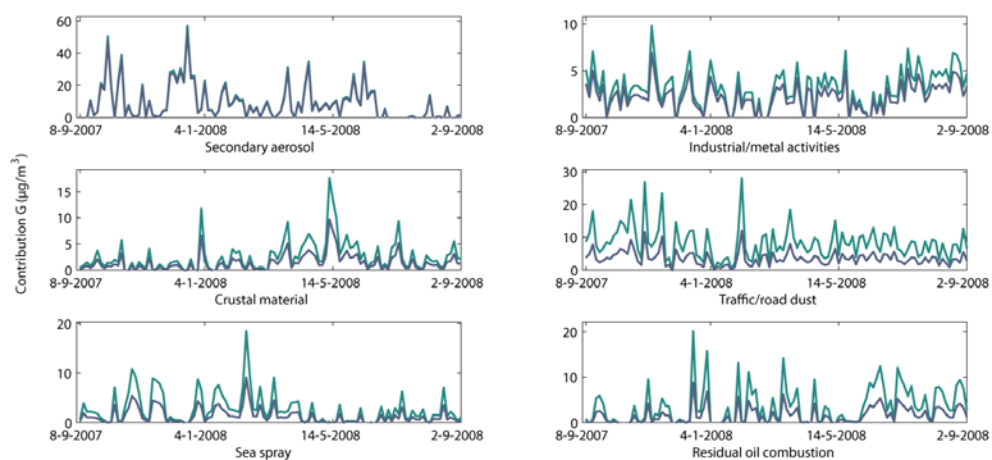


Figure 19 Time series contribution plots for six source profiles for the location at Rotterdam

The blue line represents the results for $PM_{2.5}$ and the green line for PM_{10} .

E Cabauw

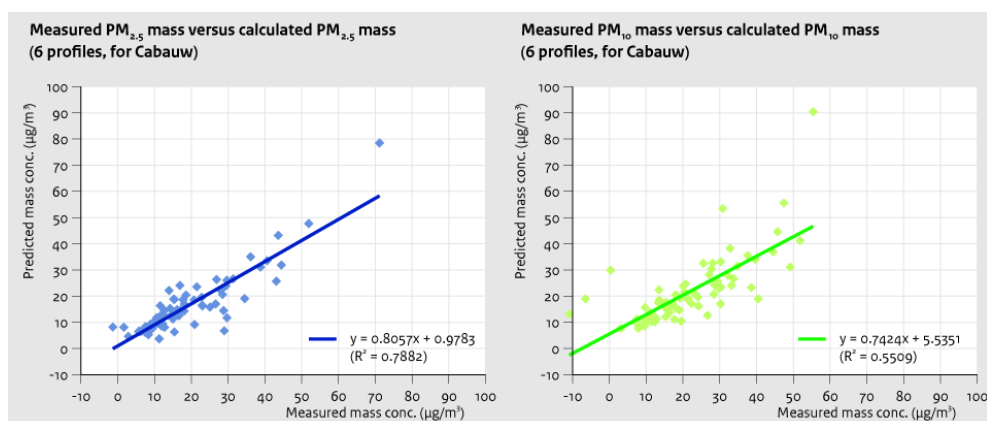


Figure 20 Comparison of measured mass and apportioned mass at Cabauw for both PM_{2.5} (left, in blue) and PM₁₀ (right, in green) data sets, based on the contributions of all six factors
The solid lines are the linear regression results.

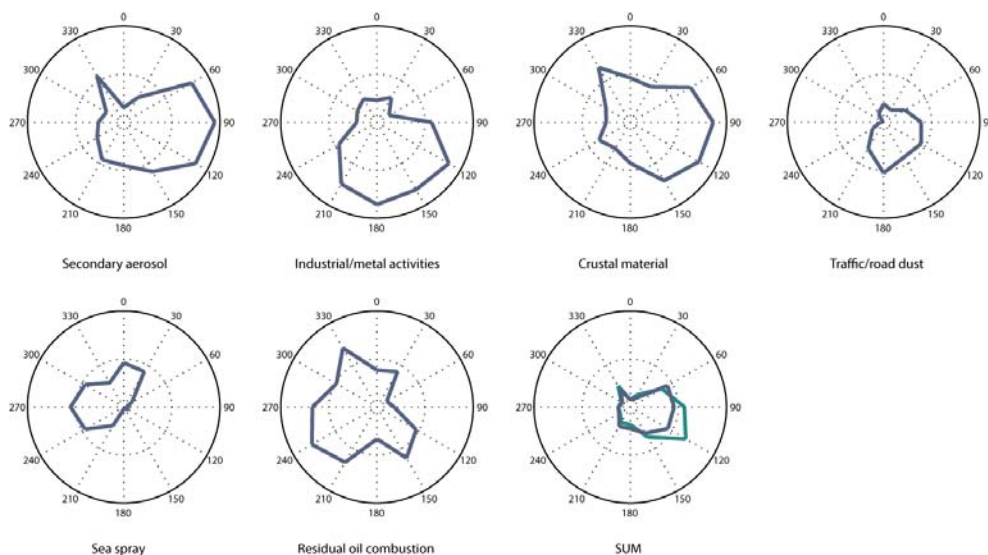


Figure 21 CPF plots for the six source profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport
The blue line represents the results for PM_{2.5} and the green line for PM₁₀.

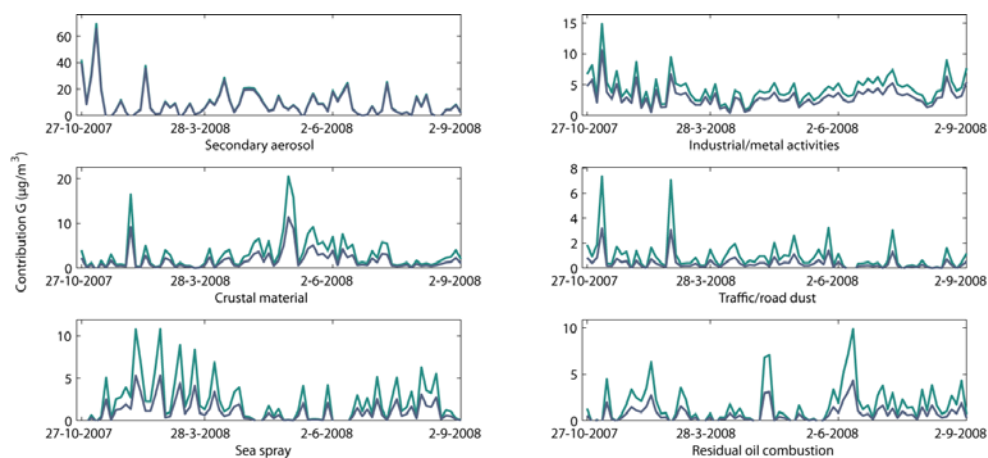


Figure 22 Time series contribution plots for six source profiles for the location at Cabauw

The blue line represents the results for $PM_{2.5}$ and the green line for PM_{10} .

F Vredepeel

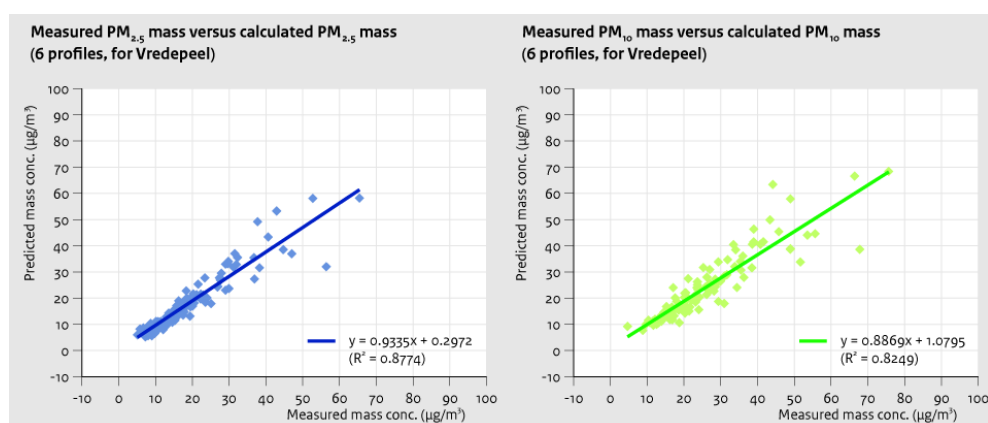


Figure 23 Comparison of measured mass and apportioned mass at Vredepeel for both PM_{2.5} (left, in blue) and PM₁₀ (right, in green) data sets, based on the contributions of all six factors
The solid lines are the linear regression results.

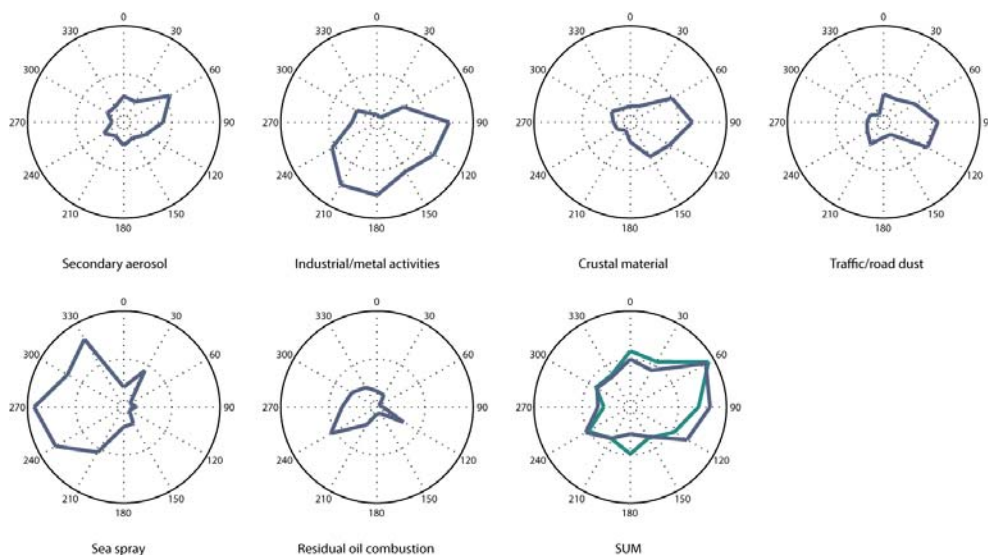


Figure 24 CPF plots for the six source profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport
The blue line represents the results for PM_{2.5} and the green line for PM₁₀.

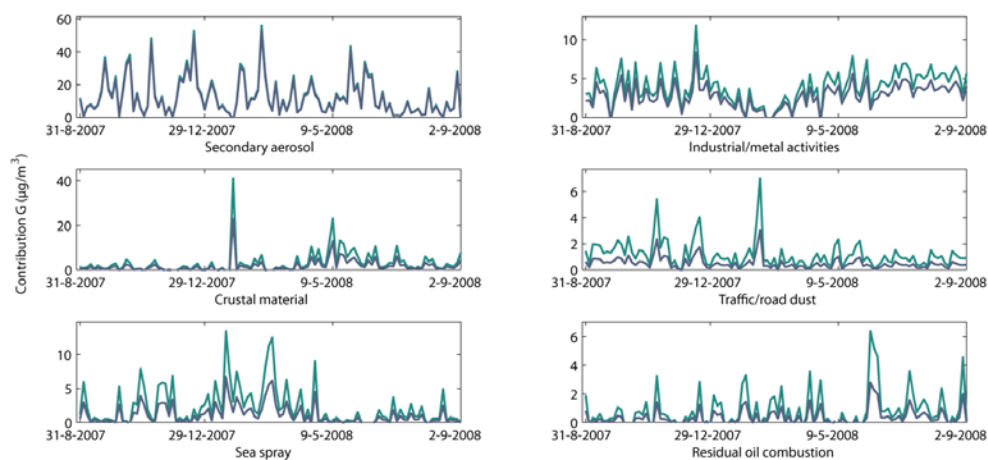


Figure 25 Time series contribution plots for six source profiles for the location at Vredepeel

The blue line represents the results for PM_{2.5} and the green line for PM₁₀.

G Hellendoorn

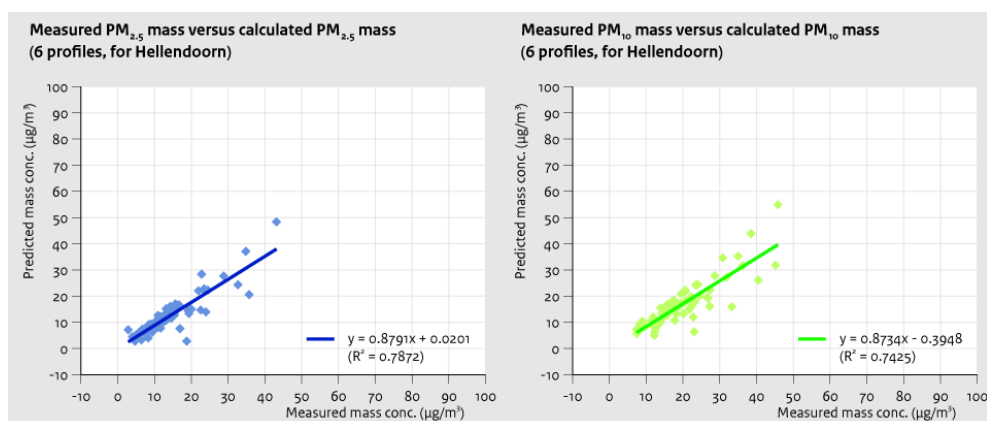


Figure 26 Comparison of measured mass and apportioned mass at Hellendoorn for both PM_{2.5} (left, in blue) and PM₁₀ (right, in green) data sets, based on the contributions of all six factors
The solid lines are the linear regression results.

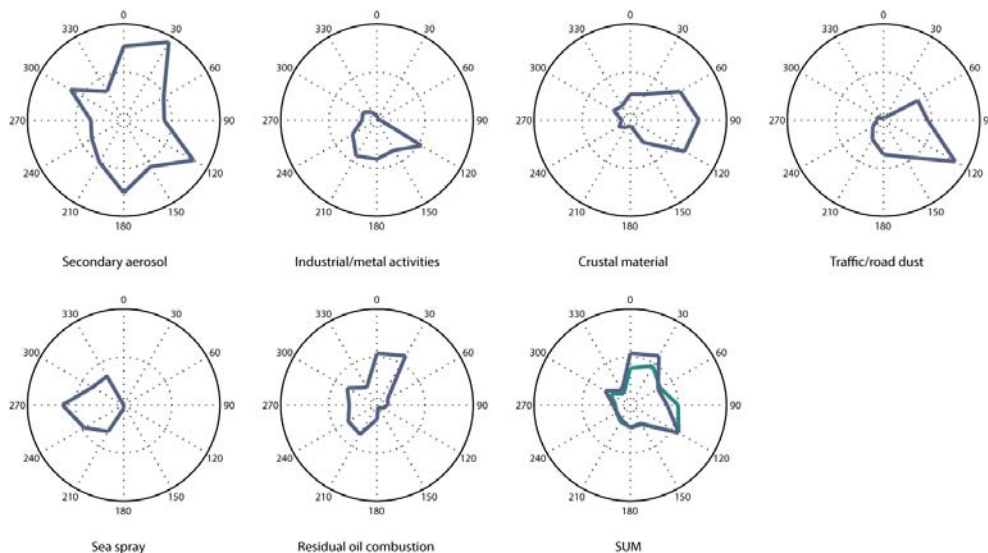


Figure 27 CPF plots for the six source profiles and for the sum of the profiles, using the wind data from meteorological station 344 at Rotterdam Airport
The blue line represents the results for PM_{2.5} and the green line for PM₁₀.

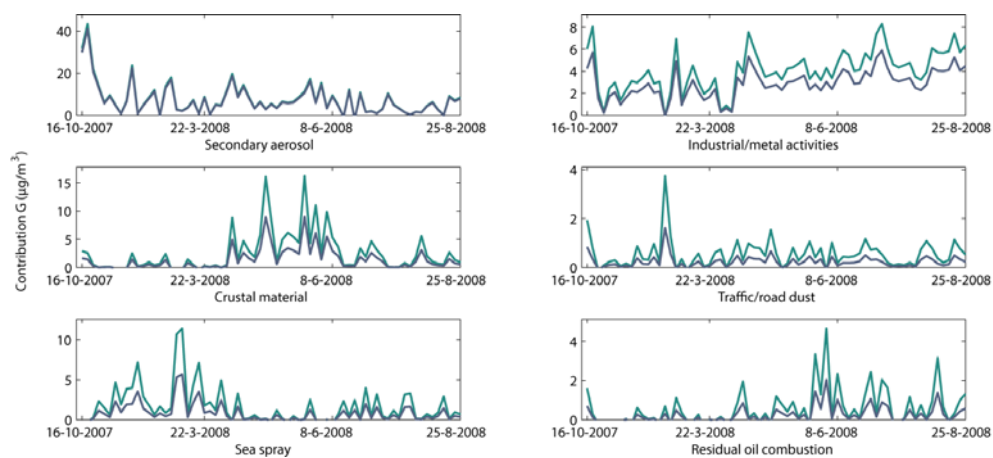


Figure 28 Time series contribution plots for six source profiles for the location at Hellendoorn

The blue line represents the results for $PM_{2.5}$ and the green line for PM_{10} .

A reanalysis of the BOP dataset: Source apportionment and mineral dust

Detailed measurements of the concentrations of particulate matter (PM) in the air have been performed from August 2007 to September 2008 at six locations in the Netherlands (the BOP dataset). During the measurements, a distinction was made between the total amount of particulate matter (PM_{10}) and its finer fraction ($PM_{2.5}$). The resulting dataset includes information on the chemical components of particulate matter. This composition provides important information about the origin of particulate matter, such as industry and traffic. Some questions about the origin of particulate matter remained unanswered after BOP. This report shows the results of a further investigation of two of these questions in the framework of BOP II.

The BOP dataset gave some differences in the composition of PM_{10} and $PM_{2.5}$ which originate from the same source. The question to be explored was how this difference can be explained. This research has shown that these differences are implicitly present in the dataset, and are not caused by the calculation method used. The cause of the inconsistencies in the dataset remains unclear, although a number of options have been excluded. The second question concerned the contribution of mineral dust to PM_{10} concentrations. According to previous calculations, mineral dust concentrations in Flanders were twice as large as compared to concentrations in the Netherlands. Here it is shown that this difference can largely be explained by the used calculation method. Therefore in this case the differences are not attributable to the measurement data.

The Netherlands Research Program on Particulate Matter II (BOP II) is a national program on $PM_{2.5}$ and PM_{10} . It is a framework of cooperation involving the Energy research Centre of the Netherlands (ECN), the Environment and Safety Division of the National Institute for Public Health and the Environment (RIVM) and TNO.

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