# Assessment of emissions of PM and $NO_x$ of sea going vessels by field measurements


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**TNO Built Environment and Geosciences**

Nederlandse Organisatie voor
toegepast-natuurwetenschappelijk
onderzoek / Netherlands Organisation
for Applied Scientific Research

Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

www.tno.nl

T +31 55 549 34 93
F +31 55 541 98 37

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|---|---|---|---|
| Date | November 2007 | | |
| Authors | Jan Duyzer | - | TNO |
| | Koos Hollander | - | TNO |
| | Marita Voogt | - | TNO |
| | Henk Verhagen | - | TNO |
| | Hilbrand Weststrate | - | TNO |
| | Arjan Hensen | - | ECN |
| | Aline Kraai | - | ECN |
| | Gerard Kos | - | ECN |

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## Summary

Emission estimates are used in air pollution dispersion models to calculate the contribution of the emission of various sources to local air quality. These sources include road transport, industry and also the emissions of sea going ships. The factors used to estimate emissions of sea-going ships to air (so called emission factors) are based upon critical evaluation of the literature. Current estimates of emission factors of seagoing ships are based upon a limited number of laboratory experiments and information on fuel usage and engine power. Especially emissions of nitrogen oxides ($NO_x$)[1] are reported in literature, measurements of particulate matter ($PM^2$) are scarcer. It is important to realize that large variations in results are observed especially in emissions of particulate matter by engines using HFO (Heavy Fuel Oil). These are therefore rather uncertain. In the process of developing scenarios to improve local air quality and decrease atmospheric deposition accurate data on emissions are essential.

The Dutch Ministry of Transport, Public Works and Water Management, Directorate General for Transport and Air Traffic (DGTL) has commissioned TNO cooperating with ECN to carry out research into emissions and emission factors of sea going ships. The objectives of the study are:
- provide insight in emission factors of PM and $NO_x$ from see going ships;
- provide insight into the impact of new and future legislation relating to the sulphur content and the emission of PM and $NO_x$.

This report shows the results of the work carried out in the project. In an earlier report the first phase of this project is described. The latter report focuses on the development of a measurement strategy. In this report the results of measurements carried out in the main phase of the project are described.
The goal of this study was therefore to provide insight in the emission factors of $NO_x$ and PM by seagoing vessels. It was the aim to improve insight by doing actual measurements. A number of methods to estimate such emissions were evaluated in the proposal phase and it was decided to evaluate different methods in the first phase. Three different cases were considered:

- emissions of ships at berth
- emissions of ships on the Netherlands continental shelf (NCP)
- emissions of ships sailing and manoeuvring in the Dutch Waterways

[1] $NO_x$ is the sum of concentrations of NO (nitric oxide) and $NO_2$ (nitrogen dioxide).

[2] PM particulate matter. $PM_{10}$ the mass of particles with a diameter smaller than 10 μm. Similar names $PM_{2.5}$ and $PM_1$ for particles smaller than 2.5 and 1 μm.

***First phase***

In the first phase of the project possibilities to derive emissions from these three categories were evaluated. It proved impossible to derive accurate emission from measurements of $NO_x$ and PM from measurements carried out on the Dutch coast. There were two causes for that:
During winds from the North-West sector the contribution of emissions of $NO_x$ and $PM_{10}$ could hardly be distinguished from the contribution of sea spray. During winds from the South-West corner the background of emissions from the United Kingdom proved problematic. Therefore it was decided to pursue this idea not further. Other methods to measure emissions at sea were estimated to be very costly and were also discarded at this stage. It was suggested to derive emission factor for ships at the NCP from measurements carried out near the Dutch coast or in canals such as the Nieuwe Waterweg and correct for the difference in engine power between open sea and these canals, where appropriate.

Two campaigns were carried out in the first phase to investigate the possibility to measure emissions of ships at berth by a new plume method. It appeared that the method could be used but that the conditions required to carry out measurements were difficult to find. This problem was related to the fluctuating influence by plumes of other sources such as cars and other ships. It proved difficult to distinguish the plume from the ship that was the subject of the study and other plumes. Measurements were also hindered by large infrastructures such as buildings. Also in view of the rather detailed study that was carried out recently which provided much information, it was decided to put no extra effort in emissions of ships at berth.

***Main phase***

Most effort in the study was put in measurements of ships sailing in the Dutch territory. A new plume method was used to this purpose. The method appeared quite useful in studies of emissions by inland ships because many individual ships can be assessed in one working day. After some preliminary tests it appeared that it was difficult to measure emissions factors of PM with sufficient accuracy and improve currently used emission factors. This process severely hindered progress in the project. Three issues are important here: the error in each individual measurement, the variation in the emission factors, and the representativity of the sample. The measurement strategy was changed to improve the situation and lower the possibility of large systematic errors in the results of individual plume measurements. Finally, by a combination of different monitors it seemed possible to estimate emissions of $PM_{2.5}$ and $PM_{10}$ with a systematic error between 20 % and a maximum of 50 %. The systematic errors in measurements of emissions of $NO_x$ are quite low as became clear from an independent study carried out in the Rotterdam harbour.
The variability of emission factors however is large, especially for PM. This is related to the large variation in for example engine types and fuel quality. This

variation is much larger than it is in emission factors for inland ships. During the campaigns carried out in the study reported here some 180 vessels were investigated. It appeared that the variation in emission factors of PM was nearly 100 % whereas it was approximately 50 % for $NO_x$. An overall average could, in principle, then have an uncertainty of 20% for $PM_{10}$ and 10 % for $NO_x$ (95% confidence interval). The sample that is taken from ships sailing into the Dutch harbours is not by definition representative, however. Some specific ship types may dominate the sample and therefore it is important to derive emission factors for different groups. In a later stage a representative estimate can then be made on the basis of statistics for this group (number of ships, sailing time etc. fuel usage) and a specific emission factor. This will reduce the number of vessels per group of course, but at the same time it is hoped that the variability within the group is smaller.

*Generalized results*

Two approaches to the data were taken.

1) Overall average emission factors

As a first approach overall average results of all measurements are presented in the small table below. In total six campaigns were carried out and the emission factors of some 180 vessels were measured. Some measurements were rejected in the QA/QC procedures. Especially PM measurements were rejected because of poor quality. This is usually caused by large fluctuations in background concentration and cannot be avoided. The averages given in the table are based upon 81 (for $PM_{10}$) to 128 (for $NO_x$) observations. Although the number of measurements is large compared to other studies it is still only a small sample of the ships entering the harbour (several tens of thousands per year). Contrary to our results for inland shipping the sample is not, as such, representative for all ships. One of the causes for this difference is that sea going vessels show a larger range of emission factors. This is related to the larger range in tonnage, engine power and type and fuel type. The observed average emission factor might be dominated by the smaller ships in the sample because these ships outnumber the larger ships. Consequently it is uncertain how representative these average results are for the large number of ships entering the port of Rotterdam. This problem is illustrated by the observation that averages observed differ for each sampling site because the fleet composition (in tonnage) passing the site differs (see table 12). With the larger vessels observed in last two campaigns the emission factor for NOx is higher. The results are therefore difficult to compare with literature data and it is difficult to draw conclusions. Therefore a different approach to the data, in which more information on vessels in the sample, is more appropriate and discussed below.

| | $PM_1$ | $PM_{2.5}$ | $PM_{10}$ | NOx |
|---|---|---|---|---|
| Overall averages | 1.7 | 2.6 | 4.7 | 50 |

2) Parameterised emission factors

In a second approach the relation between emission factor and several parameters was investigated and the results were compared with earlier estimates (as presented in EMS[3]). This study was limited to the parameters used in the EMS study. To this purpose ships needed to be classified according to classes used in EMS. Ships characteristics such as engine type and age and several parameters of each ship could be traced with the help of various sources (photographs, internet) and especially staff from the Port of Rotterdam. Unfortunately there is still a group (about 40 vessels) whose characteristics could not be retrieved within the short timescale of the project. Note therefore that the average number for all vessels provided in the table above is based on *all* vessels and the parameterised numbers are based upon roughly 60-70 % of these observations. In addition the classification should still be treated with care because the quality of the classification of ships is not validated. The results are presented in table 1.

*Table 1 Emission factors of PM and $NO_x$ in g/kg derived from this study and EMS.*

| | This study | | | | EMS | | |
|---|---|---|---|---|---|---|---|
| **4-stroke Engines** | **$PM_1$** | **$PM_{2.5}$** | **$PM_{10}$** | **NOx[1)]** | | **$PM_{10}$** | **$NO_x$[2)]** |
| S<1% | 0.8 | 1.3 | 2.5 | 39-63 | MDO | 1.6 (1.6-2.6) | 59 (42-82) |
| S>1% | 1.7 | 2.9 | 6.0 | | HFO | 3.9 (3.6-4.2) | |
| 2-stroke engines | | | | | | | |
| S<1% | 1.1 | 1.7 | 3.3 | 39-70 | MDO | 1.8 (1.8-2.8) | 88 (76-111) |
| S>1% | 3.0 | 3.9 | 6.5 | | HFO | 8.8 (8.1-9.7) | |

1) Averages observed in this study

2) Emission factor used in EMS for the period between 1995 and 2000. Emission factors for different years between 1974 and 2000 and thereafter are given between brackets.

3 A formalized Dutch approach to assess emissions of the fleet sailing in the Netherlands. See Klein *et al*. (2007)

The correlation between the age of the vessel and the emission was investigated and the following conclusions were drawn from the results:

- There is no significant correlation observable between the emission factor for PM and the age of the vessel. In EMS only a weak correlation is assumed.
- The measured emission factor for $NO_x$ in general varies only to a limited extent with the age of the vessel. It is interesting to see how the emission factor for 2-stroke engines shows a maximum for vessels built in the 1980's. This is strikingly similar to EMS estimates.

It appears also that quite a good correlation exists between PM10, PM2.5 and especially PM1 emission factors and sulphur content of the fuel. This can be understood quite well from our knowledge of the process of sulphur oxidation in the engine. Therefore it is concluded that S-content is indeed an important parameter for the emission of particulate matter and that the results of our study may be used to quantify this relationship.

*Consequences and recommendation*

As was outlined above it is difficult to draw conclusions and recommend the usage of the overall results of this study for $NO_x$ in the Dutch emission assessment protocol. Large differences between the emission factors reported here and EMS estimates for different classes were not found. The emission factors estimated in this study do not differ strongly from EMS estimates. The latter vary over the years. On average the vessels studied in our campaigns were built between 1995 and 2000. For (HFO using) two stroke engines the emission factor used for this period is 88 g NOx/kg fuel. In the measurements reported here 70 g NOx/kg fuel was observed for this class. This is lower but, in view of the uncertainty interval and the uncertainty of the classification, not really significant. For 4-stroke engines EMS estimates for this period are 59 g NOx/kg fuel whereas we observed here 39 to 63 g/kg. It should also be noted that the EMS estimates for NOx are based upon a rather large volume of literature material. At this stage it is therefore not recommended to change current estimates for $NO_x$ based upon this study only.
The emission factor for PM differs more strongly whereas at the same time emission factors in EMS are not so well based as the factors for $NO_x$. Especially the emission factor for HFO used in EMS for 2-stroke engines is rather uncertain and could be biased. It is therefore recommend to lower these estimates to values observed in this study and to use the linear dependency of S-content as observed here.

A preliminary attempt is made to estimate the impact of the results of this study on estimates of emissions of PM by shipping in the Netherlands. Based on the above, emissions of $NO_x$ were not changed.
Based on this study an emission factor of 6.5 g/kg was used to estimate emissions by shipping for the Dutch continental shelf, ships at berth in Dutch territorial waters and for ships sailing in Dutch inland waters. For all categories the emission would go down by 20 to 25 %.

The effect of SECA guidelines maximizing the sulphur content of fuel at 1.5 % was also calculated. Here a linear proportion between PM emissions and sulphur content was assumed. The proportionally was derived from the observed correlation between S content of the fuel and $PM_1$ emission factors. The effect of introducing this SECA rules would lead to a reduction of the PM emission with 10% for all three source categories.

# Table of contents

# 1. Introduction

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# 2. Results of desk studies

## 2.1 Methods

Emission factors of combustion processes emissions from ships may be determined by several methods. In our proposal to the ministry various possibilities to determine these emissions (or emission factors) are discussed. Three methods are important here:

- direct measurement of the emission on board of the ship in the funnel or otherwise
- indirect measurement
  - the emission is derived from a detailed analysis of concentration measurements on one, or preferably more, sites
  - the emission is derived from dedicated measurements of concentrations on the shore in the plume of a passing vessel (quay side[8] measurements)

The latter method is especially attractive because many ships can be measured in one day. On a suitable site the emission factor of every vessel passing by may be assessed. In one working day the emission of more than 100 inland ships was determined using this method. This is in sharp contrast to direct on board measurements that usually take at least one day per ship.
In the proposal it is attempted to achieve an optimal balance between costs, project duration and the quality of the results. The final goal is to obtain information on emissions by ships:

- Manoeuvring on the Dutch Continental Shelf (NCP)
- Sailing and manoeuvring on Dutch territory (Dutch Waterways)
- Ships at berth

In view of several uncertain factors in the approach the project was split in phases. In the first phase the technical possibilities were explored. In the second phase measurements were carried out. The results of this phase are presented and discussed here in the final report.
The results of the first phase are only discussed here as far as they are important for the final result.

## 2.2 Estimating emissions of sea going ships: The Dutch emissions inventory

In the framework of the Dutch EMS project Oonk *et al*. (2003) have given an overview of emission factors.
Table 1 and Table 3 show the estimated emission factors. Different units are used in this report to present emission factors: g/kg fuel equivalent to kg/ton fuel. Also g/kWh is used. In this unit the efficiency of the vessels engine needs to be taken into account. Since this information is often not available from each ship studied here this unit is not used in the presentations. Major factors are engine type (slow to high speed) and fuel consumption. Table 5 and Table 6 provide the same information in kg per ton fuel. The fuel type, MDO (Marine Diesel Oil) or HFO (Heavy Fuel Oil) is important and therefore specific emission factors are derived for HFO and MDO users.

*Table 2 Emission factors for low speed engines (two stroke engines) in g per kWh.*

| Year | HC | CO | $NO_x$ | PM HFO | PM MDO | Fuel Cons. |
|---|---|---|---|---|---|---|
| < 1974 | 0.6 | 3.0 | 16 | 1.7 | 0.5 | 210 |
| 1975-1979 | 0.6 | 3.0 | 18 | 1.7 | 0.5 | 200 |
| 1980-1984 | 0.6 | 3.0 | 19 | 1.7 | 0.5 | 190 |
| 1985-1989 | 0.6 | 2.5 | 20 | 1.7 | 0.5 | 180 |
| 1990-1994 | 0.5 | 2.0 | 18 | 1.7 | 0.4 | 175 |
| 1995-1999 | 0.4 | 2.0 | 15 | 1.5 | 0.3 | 170 |
| 2000 | 0.3 | 2.0 | Table 7 | 1.5 | 0.3 | 168 |

*Table 3 Emission factors for medium and high speed engines (four stroke engines) in g per kWh.*

| Year | HC | CO | $NO_x$ | PM HFO | PM MDO | Fuel Cons. |
|---|---|---|---|---|---|---|
| < 1974 | 0.6 | 3.0 | 12 | 0.8 | 0.5 | 225 |
| 1975-1979 | 0.6 | 3.0 | 14 | 0.8 | 0.5 | 215 |
| 1980-1984 | 0.6 | 3.0 | 15 | 0.8 | 0.5 | 205 |
| 1985-1989 | 0.6 | 2.5 | 16 | 0.8 | 0.5 | 195 |
| 1990-1994 | 0.5 | 2.0 | 14 | 0.8 | 0.4 | 190 |
| 1995-1999 | 0.4 | 2.0 | 11 | 0.7 | 0.3 | 185 |
| 2000 | 0.3 | 2.0 | Table 7 | 0.7 | 0.3 | 183 |

*Table 4 Correction factors on emission factors from tables 1 and 2.*

| Fractional Load | $NO_x$ | CO | HC | PM |
|---|---|---|---|---|
| 85% | 0.97 | 0.70 | 0.84 | 0.97 |
| 50% | 1.00 | 1.12 | 1.03 | 1.01 |
| 45% | 1.01 | 1.23 | 1.09 | 1.01 |
| 40% | 1.02 | 1.38 | 1.16 | 1.03 |
| 35% | 1.03 | 1.56 | 1.27 | 1.05 |
| 30% | 1.04 | 1.80 | 1.42 | 1.08 |
| 25% | 1.06 | 2.14 | 1.65 | 1.12 |
| 20% | 1.10 | 2.66 | 2.02 | 1.19 |
| 15% | 1.17 | 3.51 | 2.74 | 1.32 |
| 10% | 1.34 | 5.22 | 4.46 | 1.63 |

*Table 5 Emission factors for slow speed engines (2-stroke engines kg per ton fuel).*

| Year | HC | CO | $NO_x$ | PM HFO | PM MDO |
|---|---|---|---|---|---|
| < 1974 | 2,9 | 14 | 76 | 8,1 | 2,4 |
| 1975-1879 | 3,0 | 15 | 90 | 8,5 | 2,5 |
| 1980-1984 | 3,2 | 16 | 100 | 8,9 | 2,6 |
| 1985-1989 | 3,3 | 14 | 111 | 9,4 | 2,8 |
| 1990-1994 | 2,9 | 11 | 103 | 9,7 | 2,3 |
| 1995-1999 | 2,4 | 12 | 88 | 8,8 | 1,8 |
| 2000 | 1,8 | 12 | Table 7 | 8,9 | 1,8 |

*Table 6 Emission factors for medium or high speed engines (4-stroke engines kg per ton fuel).*

| Year | HC | CO | $NO_x$ | PM HFO | PM MDO |
|---|---|---|---|---|---|
| < 1974 | 2,7 | 13 | 53 | 3,6 | 2,2 |
| 1975-1879 | 2,8 | 14 | 65 | 3,7 | 2,3 |
| 1980-1984 | 2,9 | 15 | 73 | 3,9 | 2,4 |
| 1985-1989 | 3,1 | 13 | 82 | 4,1 | 2,6 |
| 1990-1994 | 2,6 | 11 | 74 | 4,2 | 2,1 |
| 1995-1999 | 2,2 | 11 | 59 | 3,9 | 1,6 |
| 2000 | 1,6 | 11 | Table 7 | 3,7 | 1,6 |

*Table 7 $NO_x$-emission factor for engines built after the year 2000(g per kWh).*

| RPM | $NO_x$-emission (g / kWh) | $NO_x$-emission (kg / ton fuel) |
|---|---|---|
| < 130 rpm | 14,5 | 79 |
| Between 130 and 2000 rpm | $38 \cdot n^{-0,2}$ | |
| More then 2000 rpm | 8,3 | 42 |

With respect to the uncertainty in emission factors the following is important:

- Emission factors of ships built before 1975 are rather uncertain and there is certainly room for improvement. On the other hand it should be noted the contribution of these ships is rather limited and therefore the priority for research into the emission of these ships low. Most vessels are not used after 30 years.
- Emission factors of vessels built between 1980 and 1990 have been subject to studies carried out by Lloyds in1990 (Marine exhaust Emissions research programme, Lloyds register, Croyden). These emission factors are therefore reasonably well established and new measurements will probably not lead to new insights. The emissions of PM were not measured by Lloyds however and consequently these are uncertain.
- Emission factors of ships built in the period between the Lloyds study and the introduction of the IMO standards have not been established on the basis of an extensive monitoring campaign and therefore there is a need for improvement. Especially because these vessels contribute significantly to present emissions.
- The emission factors of ships built after the introduction of the IMO standards are rather well established in the process of certification of the engines.

Summarizing it may be stated that the emission of vessels with low speed engines and especially those using HFO are uncertain and it is important that this group is well represented in the sample that is taken.

## 2.3 Literature review of particle emissions

The number of available and relevant publications was found to be only limited. Details of the literature search can be found in Duyzer *et al.* (2006).
Especially for (fine) particulates, experimental results are often difficult to compare as a result of the use of very diverse sampling and quantifying methods in their measurement. The emerging general impression becomes therefore very complex.
An important part of the literature search addressed the particle size distribution of the emitted particulate matter. As will be shown later on in this report, this is an important factor in the choice of the equipment for the measurement of the particulate emissions.
Particle counters for example, determine the number of (emitted) particles. Numbers, diameters but also particle density, then become important to transform these into mass emissions. A large number of very small particles may represent less mass than a few large ones (1000 particles with 0.1 µm diameter vs. 1 particle with 1 µm diameter). The particle size distribution is therefore an important feature of the emission.

From only limited measurements on ships diesels it turns out that the particle size distribution in the exhaust gas can be approximated by a log-normal size distribution with a number median diameter of 50-100 nm. Straight forward calculation

then shows that the mass distribution will centre at a median of 180-300 nm. Figure 1 shows an example of this relation between number and mass size distribution (taken from a car diesel engine).
Measurements with a cascade impactor (see appendix 1) sometimes show a coarse mode with a mass median diameter between 7 and 10 µm. These coarse particles seem to originate essentially from re-dispersion in the exhaust gas of agglomerates of particles first accumulated in the interior of the engine and not directly emitted by the combustion process. The contribution of these particles to the total emission is expected to be small.
The PM emissions are therefore almost completely within the $PM_1$ fraction and certainly within the $PM_{2.5}$ fraction, with only a small contribution extending into the $PM_{10}$ fraction.
This is an important finding for the design of the measurement programme and choice of monitoring equipment. The measurements should focus on the $PM_{2.5}$ (or even $PM_1$) fraction since it is not to be expected that the $PM_{10}$ fraction is much larger than these fractions.

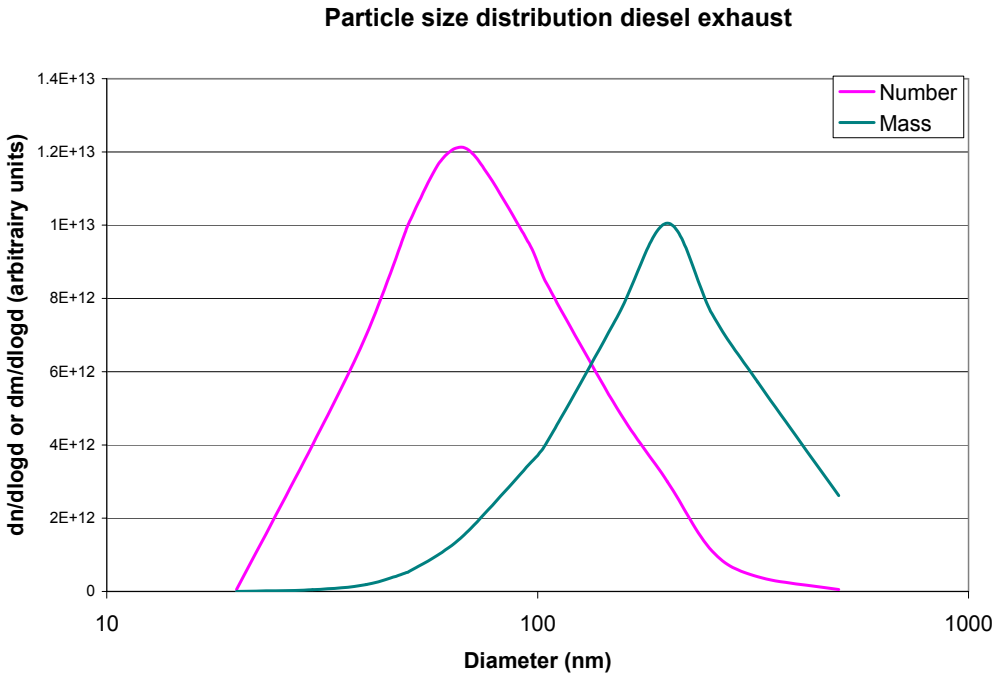


*Figure 1* *Particle number distribution according to Burtscher (2006) for car diesel engines and the particle mass distribution derived from it.*

## 2.4 Investigation of the contribution of ship emissions at the NCP to $NO_x$ and $PM_{10}$ concentrations ashore in the Rijnmond area

In the request for a quotation and the following discussion on the definition of the research proposal, the issue was raised to try to quantify (experimentally) the contribution of the ship emissions at the NCP to the air pollutant concentrations

ashore in the Rijnmond area. The TNO proposal (taking into account pressure of time and budget limits) suggested a method based on existing monitoring data. The applicability of this method has been investigated in the first phase of the study.

Duyzer *et al*. (2006) give a preliminary analysis of the estimated contributions from ships sailing at the NCP to the concentrations of $SO_2$, $NO_x$ and $PM_{10}$ in the Rijnmond area. The method used is based on measurements of the air pollutants mentioned before, at the coastal monitoring site "De Zilk", part of the National Air Pollution Monitoring Network operated by the National Institute for Public Health and the Environment (RIVM).
The contribution was derived from the average concentrations at the coastal station during wind from sea and its ratio to the overall yearly average for the site, taking into account the wind direction frequencies. This calculation gives the contributions in absolute and relative sense.

*Table 8 Contribution of the sector Southwest to North Northeast (230 - 20º) to concentrations in the Rijnmond area.*

| Component | Average | Contribution in µg/m$^3$ | Contribution in % |
|---|---|---|---|
| $SO_2$ (µg/m$^3$) | 10 – 15 | 1.53 | 10 - 15 |
| $NO_x$ (ppb) | 50 – 60 *) | 3.50 | 6 – 7 |
| $PM_{10}$ (µg/m$^3$) | 25 – 30 | 13.9 **) | 46 - 56 |

*) Excluding road side stations along busy streets.

**) Possibly overestimated because of the contribution of seasalt (7 µg/m$^3$) and sand from dunes. The wind sector 230-20º would then contribute for nearly 25% t the concentration in the Rijnmond Area.

The contribution to concentrations of $NO_x$ is small. The contribution to $PM_{10}$ on the other hand is considerable. Unfortunately, the applied simple method of analyses is not able to distinguish between exhaust emissions at the NCP and sea spray contributions to PM at the coastal station.
Considering the assessment in the framework of the Dutch Air Quality Legislation (Besluit Luchtkwaliteit 2005), a sea salt correction of 6-7 µg/m$^3$ may be applied near the coast. This means that 6 to 7 µg/m$^3$ may be subtracted from measured or calculated concentrations of $PM_{10}$ before a comparison with limit values is made. Taking into account such a contribution of sea salt to concentrations onshore, the contribution of ship emissions would reduce to about 25%.
At first, contributions of the emission at sea in the wind sectors 270-360° were investigated. This northwest sector is dominated by ship emissions of the NCP, but it also contains emissions from the North Sea, a much larger area. With respect to $PM_{10}$, the contribution to the yearly average concentration in this sector is hardly larger than the estimated contribution of sea salt. The difference is so small, that a comparison with model calculations will be of little help.
In a second calculation the contribution of the south western part of the NCP was included. The contribution to $PM_{10}$ significantly increases to 13.9 µg/m$^3$ in this case. This is thought to result from emissions of ships manoeuvring near the harbours. However, this contribution was found unrealistically high. Mathijsen en

Visser (2006) calculated for the whole NCP a contribution of 1.4 $\mu g/m^3$. The large divergence between the two estimations is thought to be due to emissions from the UK part of the NCP and from the UK itself.
It looks almost impossible to distinguish the individual contributions of the NCP, the UK part of the CP, the UK itself and the North Sea using these measurements.

*Proposal for further research:*
To investigate the quality of the current emission factors, concentrations of $NO_x$ and fine particulate matter ($PM_{10}$) in the Rijnmond area could be modelled, based on current emission factors and an estimate of ship movements on the NCP. Comparison between calculated and measured concentrations could show the adequacy of the emission factors.
The analysis presented above allows the following conclusions:
The sector north-west, with almost only contributions of ship movements on the NCP, contributes negligible to the concentrations of $PM_{10}$ in the Rijnmond area. The contribution is so small (and therefore inaccurate) that a comparison between modelled and measured concentrations would be inconclusive with respect to the PM emission factors.
Without further analyses it is concluded that similar conclusions hold for $NO_x$ and $SO_2$. Moreover the importance of a similar analysis is regarded less important for these air pollutants.
For the whole south-west to north-west sector a much larger contribution to the concentrations of $PM_{10}$ in the Rijnmond area is estimated, based on air quality measurements. The large size of this contribution leads to the expectation that there is a considerable contribution from emissions in the UK and the UK part of the CP.

Based on these conclusions it was proposed not to continue this analysis at this stage but give priority to other parts of the project.

# 3. Investigation of experimental methods to determine the emissions of sea going ships

## 3.1 Introduction

As was discussed above, the indirect downwind plume method (as opposed to the direct in stack emission measurement) was used. Shortly this implies the following:

*Downwind plume method, general (quayside method):*
Monitoring equipment is installed along the waterside, downwind from the passing ships. In the ideal case the wind direction is almost perpendicular to the waterway. When a ship passes, the exhaust gas plume of the mobile source (the ship) traverses the stationary monitoring equipment (equivalent to traversing the plume of a stationary source with mobile monitoring equipment) and the concentrations of the emitted air pollutants will temporary increase above the background. This results in a concentration – time profile, equivalent to the plume profile. From the concentrations of for example $NO_x$, $SO_2$ and PM in the plume, rated against the simultaneously measured $CO_2$ concentration ($CO_2$ to be used as a tracer of the fuel consumption, power load of the ship), the emissions are calculated from the ratio of concentrations of the pollutants over the concentration of $CO_2$. Figure 2 shows an example of the complete measurement cycle.
An independent project in which this method was compared with the classical method was carried under contract with the Port of Rotterdam. In three complete measurement cycles the emission of $NO_x$ was measured in the ships funnel as well as on the shore using. In all three the difference between the results of the method was less than 15% and less than 10% on average (see Appendix 3 for the results).

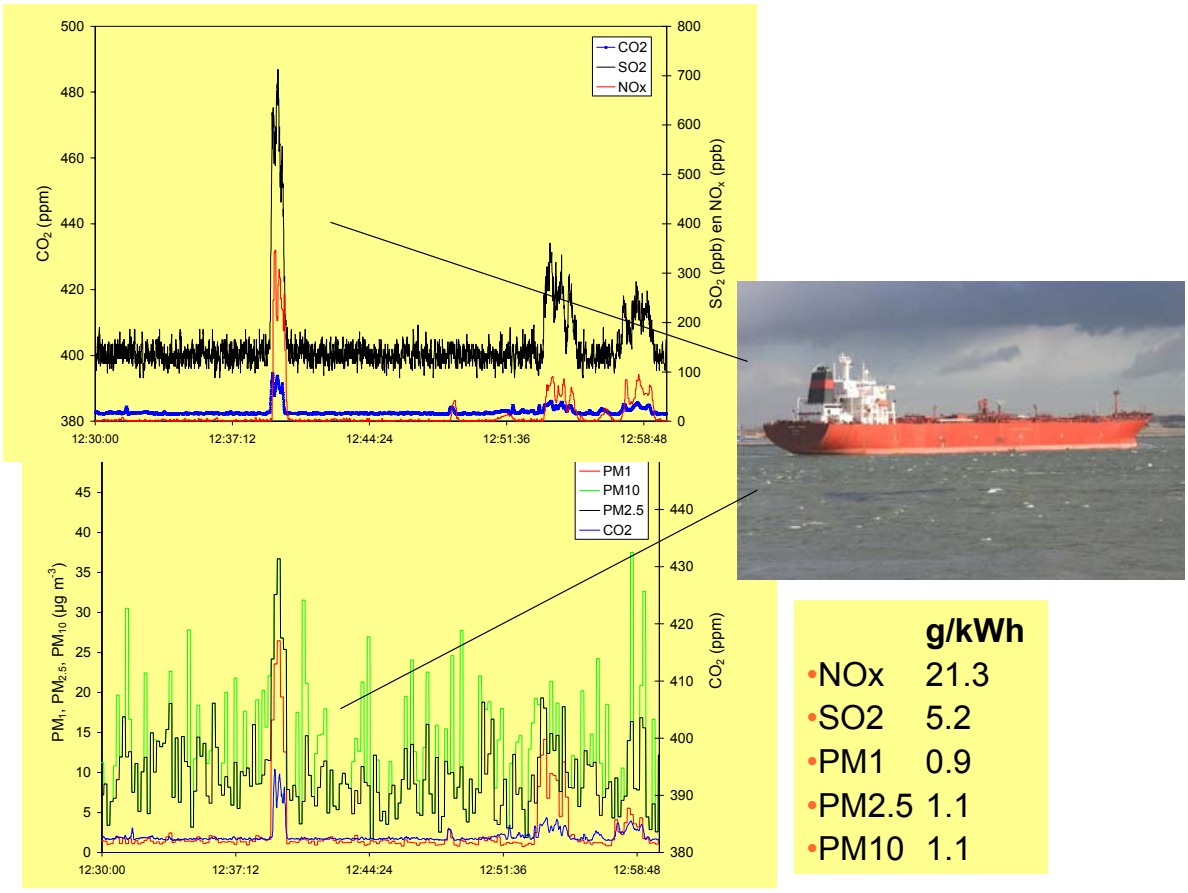


*Figure 2* *Example of a complete measurement of one vessel showing the peaks in concentration of $CO_2$, $SO_2$ and $NO_x$ (top diagram) and $PM_1$, $PM_{2.5}$ and $PM_{10}$ in the lower diagram. The emission factor derived from this graph is shown right corner below.*

*Downwind plume method for particulate matter*

The measurement of gaseous emissions like $NO_x$ and $SO_2$ runs exactly as described above. The measurement of PM requires some additional steps. This relates to the measurement technique. The plume of a passing ship is measurable during a few tens of seconds. Monitoring instruments for gasses are fast enough to perform this task. Mass monitoring instruments are not fast enough to do so. There are however fast instruments which measure total particle numbers ($n/m^3$). Some of them are even able to classify particles in a number of size classes (a little less fast). When particles would be spheres and their density known, the particle size distribution could be converted to particle mass ($\mu g/m^3$). However, the assumption of spherical particles is not generally justified and their density badly known and probably dependent of their diameter. It may vary from 0.7 to 1.6 $g/cm^3$. This may give a considerable (systematic) uncertainty. To circumvent this uncertainty a combined approach is chosen:

– The emission is measured with a fast particle counter. The counter classifies the particles according to their size. The diameter range is from 30 nm to a few

micrometers. The instruments used were a LAS and ELPI (see appendix 1 for a description of all instruments).

– Aerosol mass is measured with a slow mass monitor (TEOM with $PM_{10}$ or $PM_{2.5}$ inlet). This number is also used to calibrate the fast particle counter.

The two monitors are used simultaneously. Together they provide on the one hand the particle numbers in several size classes and on the other hand the mass concentration (TEOM). The density of the counted particles is adjusted so that the mass calculated from the particle number distribution matches the measured mass concentration from the TEOM.
The TEOM (certified according to EN12341) is valid in the Netherlands as a secondary standard for mass monitoring. As it is expected that ship emissions consist largely of $PM_{2.5}$ or $PM_{1.0}$, the match with particle counters may be improved by monitoring specifically these fractions with the TEOM. This way the emission factor in mass units is derived on the basis of this internal calibration. Figure 3 provides an example of the calibration using the TEOM slow response monitor on the 1st of September 2006. The concentrations compare quite well with differences typically less then 20%. Also during other campaigns monitors were compared.

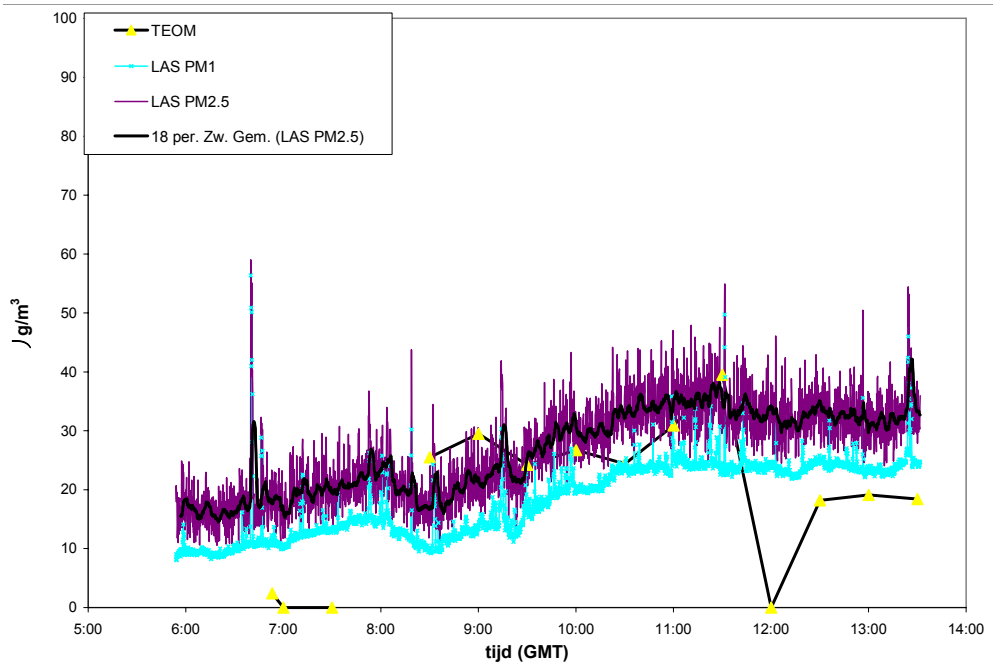


*Figure 3* *Comparison between PM concentrations derived from the fast response LAS particle counter compared with concentrations measured with the TEOM slow response reference monitor (equipped with $PM_{2.5}$ Head). Starting on 12:00 the TEOM was equipped with a $PM_1$ inlet (1 September 2006).*

Similar results were obtained during the campaign carried out on the 7th of November as is shown in Figure 4. Again the comparison between TEOM and LAS is quite good and from the order of 16 % maximum (with the LAS estimating the highest concentrations).On the 2nd of November 2007 the comparison was of lesser quality. During moderate to strong northerly winds the TEOM (operating in the FDMS mode i.e. counting only non volatile matter) saw very low background concentrations in the $PM_{2.5}$ range. The particles seen in vessels plumes were too low to enhance the background as observed by the TEOM. The difference with the fast counting OSIRIS was on average 11% (with the Osiris estimating lower particle mass). The results of this campaign are shown illustrated in Figure 5.

In an additional attempt to evaluate the accuracy of the measurements with the LAS particle-counter, samples were taken with an impactor. Here particles of a particular size are sampled on a filter. Unfortunately samples need to be of a certain minimal size. Only then the weight of the filter is sufficiently increased for it to be weighed using an analytical balance. Consequently it was not possible to determine aerosol mass for the smallest particles separately. This would have been most interesting because these fine particles are expected to determine the emission factor for diesel engines. Because of the same arguments it appeared impossible to obtain enough sample-material to take more than one sample per day. Table 8 shows the results of these measurements. In most cases the comparison between impactor measurements and both LAS and TEOM is quite good and within 15 %.

*Tabel 9* *Comparison between particle number concentrations measured by the LAS particle counter during different campaigns in a specific size compared with impactor filter measurements. The impactor measurements on 14 July were unreliable.*

| **Campaigns** | **Particle concentration ($\mu g\ m^{-3}$) by LAS counter in range 0.16-8 $\mu m$** | **Impactor stage concentration ($\mu g\ m^{-3}$) range 0.16-8 $\mu m$** | **Particle mass in ($\mu g\ m^{-3}$) determined Teom. Between brackets the size ranges** |
|---|---|---|---|
| 14 July 06 | 19.4 | (8.5) | 20 ($PM_{10}$) |
| 1September06 | 25 | Nd | 29 ($PM_{2.5}$) |
| 2 November 06 | 7.8 | 9.2 | |
| 7-November 06 | 48.2 | 52.6 | 40 ($PM_{2.5}$) |
| 23-January 07 | 14 | Nd | 7.8 |
| 24-January-07 | 6.8 | 3.1 | 4.9 |

*Nd = no data*

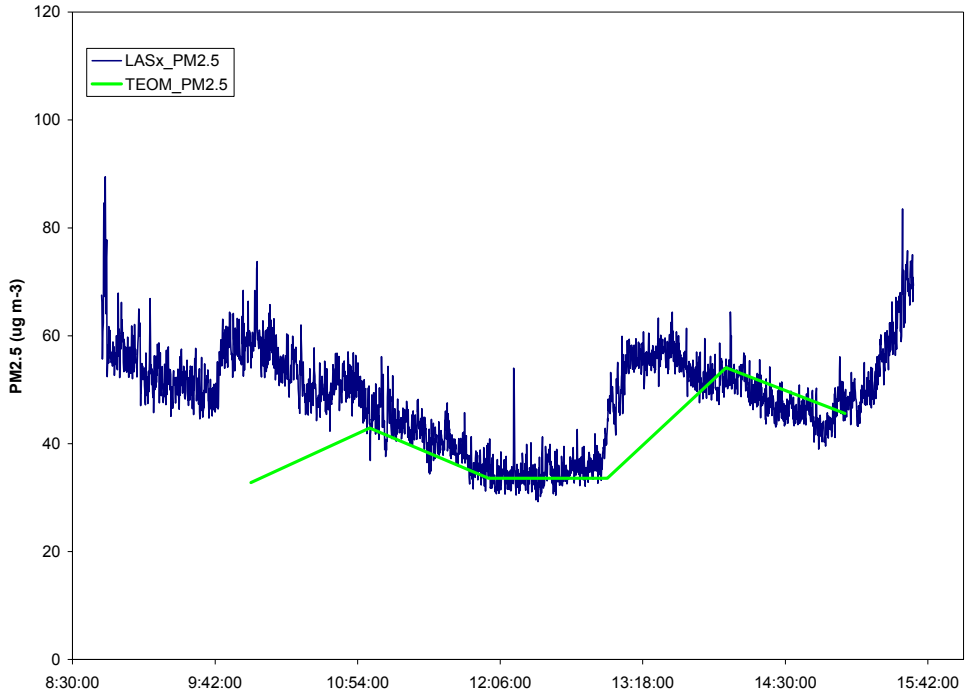


*Figure 4* *Comparison between PM concentrations derived from the fast response LAS particle counter compared with concentrations measured with the TEOM slow response reference monitor. TEOM was equipped with a $PM_{2.5}$ inlet (7 November 2006).*

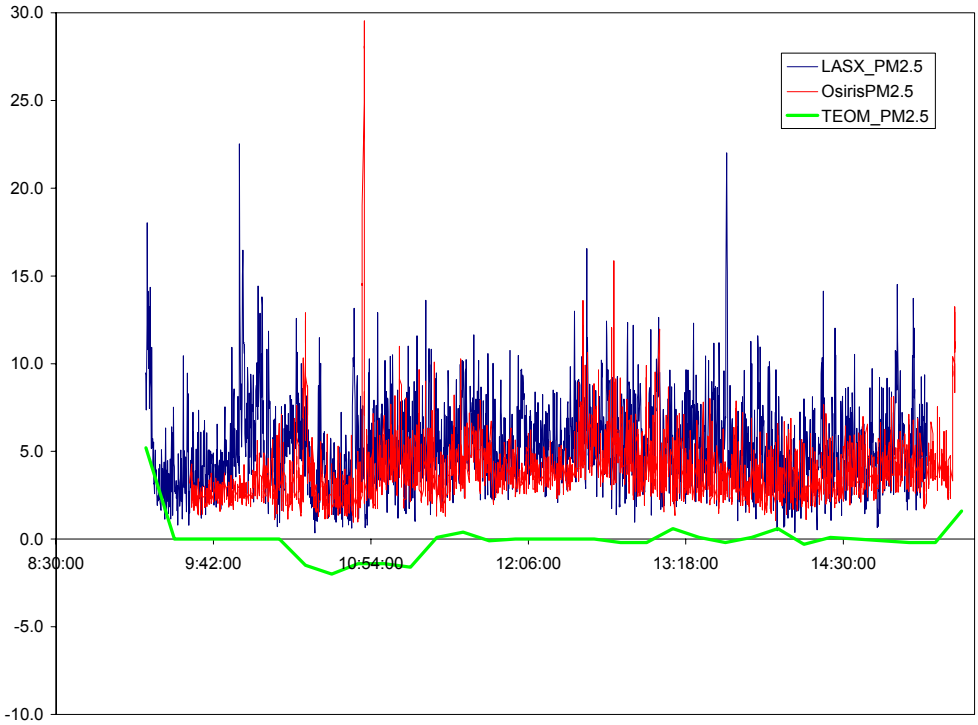


*Figure 5* *Comparison between PM concentrations derived from the fast response LAS particle counter and the Osiris particle counter compared with concentrations measured with the TEOM slow response reference monitor. TEOM was equipped with a $PM_{2.5}$ inlet (2 November 2006).*

# 4. Results of campaigns

## 4.1 Introduction

In Duyzer *et al.* (2006) a comprehensive analys was made of the strategy to obtain representative data for ships entering the Rotterdam harbour. This included statistical analyses of the types of vessels, the routes they take entering the harbour etc. These analyses provided useful guidelines as to which conditions were optimal. Nevertheless it proved difficult to carry out these measurements in practice. Weather conditions were often suboptimal making it difficult to decide whether it was a good choice to go out into the field or waste one of a limited number of budgeted days.
Vessels heading for berth in the harbour can enter the Nieuwe Waterweg, take the Calland Canal or go to the ECT terminal through the Beer Canal. As was discussed in Duyzer *et al*. (2006) the distribution of tonnage differs along these routes.


*Figure 6 Map of the Rotterdam harbour area.*

With northerly winds, measurements could be carried out at the Papagaaiebek. Under these conditions all ships entering the harbour could be investigated. Some ships however would pass at rather large distance. With southerly winds measurements were carried out on the Northern side of the Nieuwe Waterweg in Hoek of Holland. Under these conditions, only few of the interesting group of larger vessels were passing. Therefore northerly winds were considered optimal. These conditions may however be coupled with a rather high wind speed. At these conditions plumes may become very dilute and hardly detectable.
Up to now, seven campaigns were carried out in the project. All were carried in the Rijnmond area along the Nieuwe Waterweg. The 5$^{th}$ campaign organised on November 29 turned out a major disaster because the equipment put out on the dam in Hoek of Holland was flooded.

*Table 10 Overview of the measurements carried out in the project showing wind direction and the number of plumes investigated. Some plumes were rejected for several reasons In this table all plumes with a sd less than 100% were accepted. Locations see also Figure 6.*

| Campaigns | Location | Wind direction | Number of successful plume measurements | | |
|---|---|---|---|---|---|
| | | | $NO_x$ | $SO_2$ | PM |
| **14-Jul-06** | **Nieuwe Waterweg** | **N** | 17 | 14 | 13 |
| **1-Sep-06** | **Hoek van Holland** | **ZW** | 44 | 42 | 41 |
| **2-Nov-06** | **Papagaaie bek** | **N** | 24 | 21 | 16 |
| **7-Nov-06** | **Hoek van Holland** | **Z-ZW** | 29 | 26 | 9 |
| **23-Jan-07** | **Papagaaie bek** | **N** | 20 | 20 | 20 |
| **24-Jan-07** | **Papagaaie bek** | **N** | 22 | 19 | 20 |
| | | Total | 156 | 142 | 119 |

## 4.2 Data analysis

*Data treatment*

Considerable effort was put into analysis of the raw data. Especially the results of particle counts are complex to analyse. Where the number of $PM_1$ particles is quite large the number $PM_{10}$ particles is orders of magnitude smaller. The statistical uncertainty of a measurement of the $PM_{10}$ concentration in a plume (and therefore typically in only 30 seconds or so) is therefore large and the $PM_{10}$ signal is consequently very noisy. It is therefore difficult to identify the ships plume in the noisy (background) signal. This complicates the analysis of the signal an derive an emission factor for $PM_{10}$. Several methods were tested. Finally the following method was chosen:

- The exact position (the timing) of the vessels plume was derived from the $PM_1$ signal. When there was no plume detectable in the $PM_1$ signal, the plume was not considered at all. Then the error in each plume measurement ($PM_1$, $PM_{2.5}$ or $PM_{10}$) was derived from the measurements before and after the peak caused by the ships plume. So an estimate of the error was available for each individual plume.
- From this information it was decided whether a significant emission estimate could be derived or not. It was decided to use only measurements with a signal twice the standard deviation (noise) in the background. This is important for the $PM_{2.5}$ and especially for $PM_{10}$ emissions. If it was decided not to use the $PM_{2.5}$ emission it was, by default, set equal to the $PM_1$ emission. A similar procedure was used for $PM_{10}$ emission default set equal to the $PM_{2.5}$ emission. These however remain uncertain. Different data treatment could lead to slightly different results. Consequently the $PM_{10}$ emission factors are uncertain and could even be biased in one

direction. One should also bear in mind that the expectation was that most particles would be of size class $PM_1$ (see § 3.4).
- A few emission factors derived for $PM_{10}$ were rejected when the error was larger than 10 g/kg. This was only the case with a few outliers.

This is a quite common procedure. Sulphur emission factors and S contents of the fuel derived from that where also used as a proxy for the fuel type. Therefore in some of the analysis a higher error in the S estimates was allowed. This was done with the purpose not to lose relevant PM or $NO_x$ data.for the simple reason that there were no data for sulphur. Usually these high errors are associated with low sulphur content of the fuel and using these data is not relevant for the outcome of the overall analysis.

*Identification of ships and ships properties*
During the campaigns pictures were taken of each vessel passing by and names and IMO numbers were noted where possible. Based on this information additional information on the vessels was sought. Most information was obtained from the Port of Rotterdam (Ron van Gelder). This included tonnage, information on engine type, year of introduction etc.
These data were coupled with the results of the individual measurements and statistically analysed in a search for factors driving the emission of the compounds of interest.
This is a difficult process because many factors may influence emission factors. Known factors are:

- Engine type: High speed, medium or slow speed and four or two stroke engine types. These data were obtained from information provided by the port of Rotterdam. Not all information could be found unfortunately.
- Fuel type. An important distinction is marine diesel oil (MDO) and heavy fuel oil (HFO). Derived from information obtained in the EMS study and expert judgement.
- Age of the vessel (or better the engine). In some periods in the last century it was important to limit fuel usage. This may have lead to larger emissions of $NO_x$. The information on vessel age was obtained from the Port of Rotterdam and the internet.

Of these parameters nearly 80 % of the data was found. Further, it is important to realize that some of these parameters are coupled. Engine type may be coupled with the type of fuel used. Slow speed engines (usually two stroke) are more likely to use HFO. Engine speed and type and maximum power may be coupled as well. With very few exceptions all vessels with 2-stroke engines were classified as users of HFO.
Another problem is the limited information available on vessels as they pass the monitoring site. With the help of the Port of Rotterdam the crew of a few ships was interviewed to obtain this information. The number of ships that could be investigated by this method however is limited. Consequently the type of engines running,

or the actual fuel usage at the time the monitoring site was passed remains unknown at this stage (see Appendix 2 as well).
As a result of this situation the analyses was focussed on the limited information that was available and of reasonable quality. This included year of introduction, motor type (two or four stroke) and fuel type. Fuel type as such was not used. As was discussed above the uncertainty in this classification is rather high. As a proxy the emission factor of sulphur was used. It is assumed that all sulphur in the fuel is oxidised to sulphur dioxide and the emission factor therefore is proportional to sulphur content of the fuel. From a legislation point of view the sulphur content could even be more informative than the fuel type. Especially in the current study where little information on fuel type is available, sulphur content is more relevant.
Relevant statistical data of our campaigns are given in Table 10. The average year vessels, that were seen in this study, were introduced is 1995 whereas the median year of introduction is 1997. The vessels are typically 10 years old therefore.

*Tabel 11 Statistical data of all campaigns. See text for uncertainty on the listed parameters.*

| | Number of vessels | Number with estimated S content in fuel over 1 % |
|---|---|---|
| 4-stroke engine | 98 | 36 |
| 2-stroke engine | 39 | 24 |
| MDO users | 62 | 17 |
| HFO users | 36 | 19 |

*Average results*
Table 11 contains average information of all campaigns. Several interesting features may be observed in this table. First of all the average sulphur content of the fuel used is rather low and could be a result of the fact that the sample of ships is not representative.
In principle the table 11 provides the final results of this study. The confidence interval of the average emission factors is around 20 % for the particle emission factors and even much lower for $NO_x$. This suggests that the sample taken is rather good. In principle a limitation could be that measurements were only carried out during the day. But there is no reason to assume that this would lead to biased estimates. There is no indication either that days on which measurements were carried out were not typical for the Rotterdam harbour. Still it remains unclear to what extent the sample of vessels that was obtained is representative. Therefore a more detailed analysis was carried out with the purpose to obtain emission factors for specific categories. These could be used to make a more representative estimate of total emissions based on statistics of vessels visiting the Rotterdam Harbour. The analysis is discussed below.

As is shown in table 10 there is a slight overrepresentation of smaller vessels. Therefore it is difficult to discuss the results in comparison with EMS estimates. These are given for specific categories. It is interesting to see that the last

campaigns show higher emission factors for sulphur. During these campaigns more larger vessels were observed. These would normally be using HFO with a higher sulphur content.

*Tabel 12 Average emission factors and standard deviations of all campaigns obtained in the current study. The sulphur content was derived from the measured emission factor of $SO_2$ assuming that 1% S content leads to 20 g $SO_2$. Emission factors with a value smaller than twice the noise level were removed from the analysis (see text).*

| | | $NO_x/CO_2$ g/kg fuel | $SO_2/CO_2$ g/kg fuel | S% | $PM_1$ g/kg fuel | $PM_{2.5}$ g/kg fuel | $PM_{10}$ g/kg fuel |
|---|---|---|---|---|---|---|---|
| July 14 | Number | 11 | 7 | 7 | 6 | 5 | 5 |
| | Average | 41.1 | 11.4 | 0.6 | 1.5 | 0.8 | 2.6 |
| | Stdev | 18.5 | 11.7 | 0.6 | 1.9 | 0.4 | 4.4 |
| September 1 | Number | 42 | 30 | 30 | 37 | 36 | 36 |
| | Average | 36.1 | 13.8 | 0.7 | 1.3 | 1.9 | 3.2 |
| | Stdev | 18.3 | 12.4 | 0.6 | 1.1 | 1.7 | 2.8 |
| November 2 | Number | 15 | 14 | 14 | 14 | 13 | 10 |
| | Average | 53.8 | 24.8 | 1.2 | 3.1 | 6.1 | 7.7 |
| | Stdev | 28.7 | 11.3 | 0.6 | 1.3 | 3.5 | 3.4 |
| November 7 | Number | 24 | 16 | 16 | 5 | 5 | 5 |
| | Average | 39.2 | 11.2 | 0.6 | 2.7 | 4.3 | 5.7 |
| | Stdev | 24.1 | 11 | 0.5 | 2.3 | 2.9 | 3.6 |
| January 23 2007 | Number | 19 | 16 | 16 | 16 | 16 | 15 |
| | Average | 63.3 | 26.4 | 1.3 | 1.0 | 1.3 | 4.3 |
| | Stdev | 20.3 | 11.7 | 0.6 | 0.7 | 0.7 | 3.9 |
| January 24 2007 | Number | 17 | 8 | 8 | 16 | 16 | 10 |
| | Average | 87.3 | 46.4 | 2.3 | 2 | 2.4 | 8 |
| | Stdev | 49.2 | 20.4 | 1.0 | 1.3 | 1.4 | 8 |
| Total | Number | 128 | 91 | 91 | 94 | 91 | 81 |
| | Average | 50 | 19.9 | 1.0 | 1.7 | 2.6 | 4.7 |
| | Stdev | 31.7 | 16 | 0.8 | 1.4 | 2.5 | 4.5 |
| | Median | 45.1 | 21.1 | 1.1 | 1.2 | 1.7 | 3.5 |
| | Relative standard deviation | 63% | 80% | 80% | 85% | 97% | 96% |
| 95% Confidence interval (in % of mean) | | 11% | 17% | 17% | 17% | 20% | 21% |

*Results for specific categories*
The EMS classification is followed in the analysis. The sulphur content of the fuel is derived from the measured emission factor for sulphur. Then it is assumed that vessels may be considered HFO users when the fuel they use contains more than 1.0 % S. The average emission factor derived for PM and $NO_x$ may then be compared to EMS estimates (see also Appendix 2 for a discussion of the sulphur measurements).

Figure 7 shows the emission factor of $PM_1$, $PM_{2.5}$ and $PM_{10}$ derived from the measurements for 4-stroke engines. First it is important to note that the emission factor for $PM_{10}$ is some 50 % higher than the one for $PM_{2.5}$ which is again higher than the factor for $PM_1$. This is a larger difference than expected. It was to be expected that most emissions by ships would be in the $PM_1$ size range. A rather clear relation with sulphur content (derived from our measurements) is observed for this range. Here we use the sulphur content as a proxy of fuel type (see also Appendix 2 where this assumption is justified) The emission factor for the category 4-stroke HFO is higher than the one used in EMS i.e. around 6 compared to 4 kg/ ton fuel according to Table 6). The emission factor for $PM_{10}$ of fuels with lower S content (MDO) lies around 2.5 kg/ton and is therefore also little higher than the EMS value of 2 kg/ton or even less (Table 6) Note that the uncertainty is rather high for the higher S classes ( at 1.75 % S) because the number of samples is low. This is understandable because 4-stroke engines are more likely to use MDO. Because of this regression lines were not calculated.

A similar relation is observed for 2-stroke engines (see Figure 8) unfortunately the number of measurements is rather low as well. The relation with S content is probably less pronounced because of this. Although the $PM_1$ and $PM_{2.5}$ emissions are similar to 4-stroke engines the $PM_{10}$ emission factor, at low sulphur content is much higher for 2-stroke engines This could be statistical uncertainty but could be related to the usage of different fuels by these engines. Table 13 shows the average figures for this item. Unfortunately the number of ships with S content above 1.5 % is low. Compared to EMS the $PM_{10}$ emission factor for MDO is higher (3.3 kg /ton compared to 1.8 kg/ton in EMS) but significantly lower for HFO users (6.5 compared to 8.8 kg/ton used in EMS).

The influence of sulphur content on PM emissions is quite clear. An interesting difference is a rather low estimate for 2-stroke HFO (sulphur >1%) users. A similar difference is observed for 4-stroke HFO (sulphur >1%) users although the uncertainty in the estimate is much larger (see table 12). It is also obvious that the emission factors of $PM_1$ can be measured much better. Probably as a result of that the correlation with sulphur content is much stronger for $PM_1$ then it is for $PM_{10}$. It is also reasonable to assume that the effect of sulphur would indeed only be present in the $PM_1$ class. Here particles would be formed from sulphuric acid. Emission of larger particles are probably not related to sulphur content but rather to mineral material and ashes in the fuel (see § 2.3).

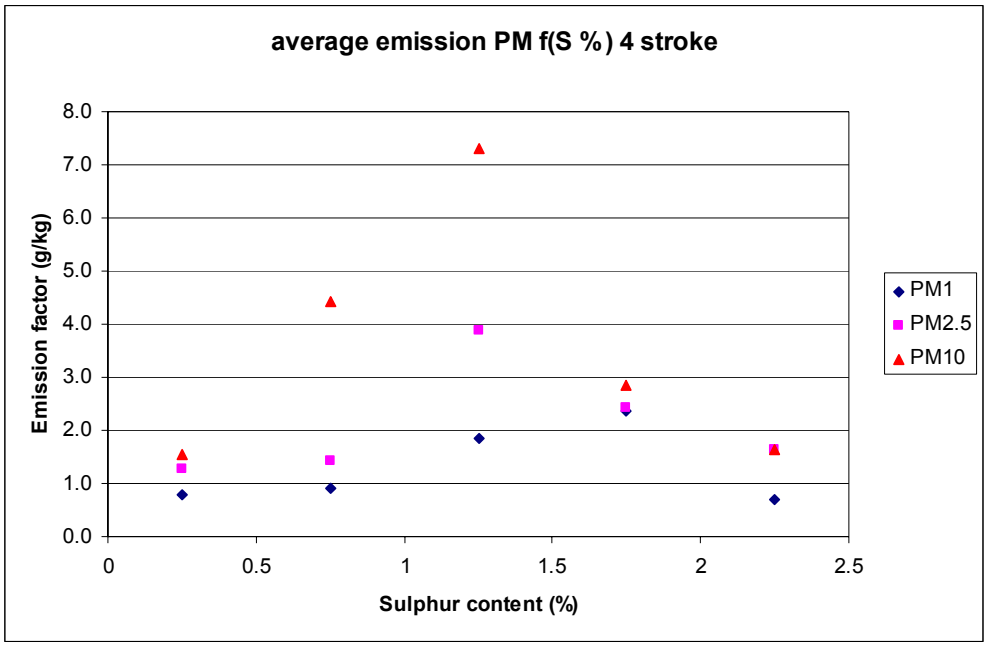


*Figure 7* *Emission factor of PM as a function of sulphur content (derived from sulphur emission factors) for 4-stroke engines.*

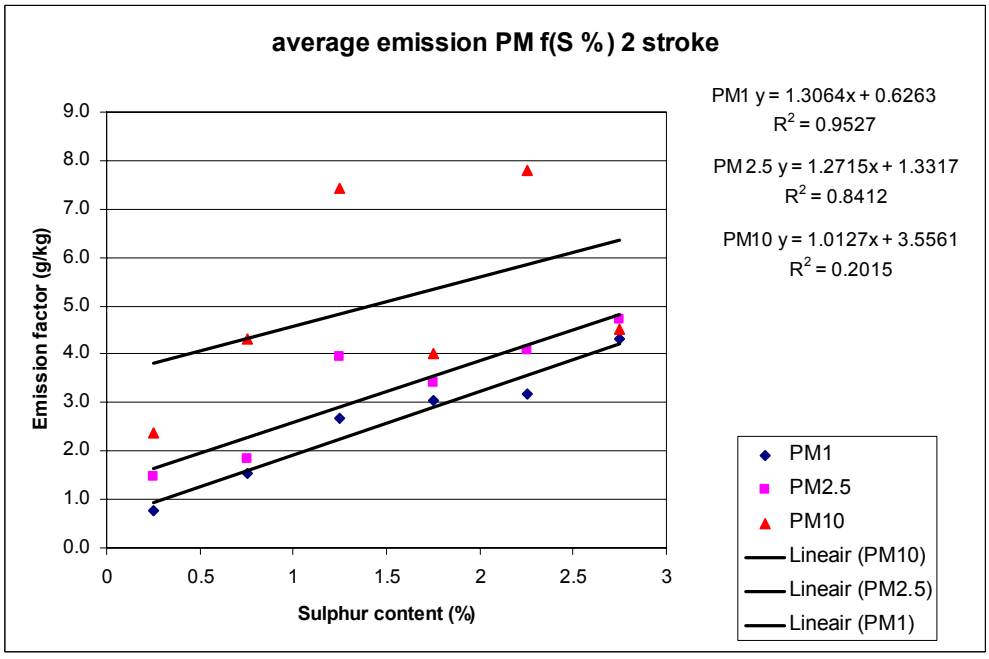


*Figure 8* *Emission factor of PM as a function of sulphur content (derived from sulphur emission factors) for 2-stroke engines.*

*Table 13 Emission factors for PM for 2 and 4stroke engines for S contents higher and lower than 1 %. Average, standard deviation and 95% confidence intervals are given.*

| | Emission factors g/kg fuel | | | | | |
|---|---|---|---|---|---|---|
| **4-stroke engines** | **$NO_x$** | **$SO_2$** | **S%** | **$PM_1$** | **$PM_{2.5}$** | **$PM_{10}$** |
| Number | 60 | 70 | 70 | 44 | 43 | 38 |
| Average | 52.1 | 18.6 | 0.9 | 1.3 | 2.2 | 4.3 |
| Stdev | 21.8 | 12.4 | 0.6 | 1.1 | 2.6 | 5.4 |
| 95% confidence interval | 11% | 16% | 16% | 26% | 35% | 41% |
| | | | | | | |
| 4-stroke S<1% | | | | | | |
| Number | 28 | 37 | 37 | 19 | 19 | 18 |
| Average | 39.5 | 8.8 | 0.4 | 0.8 | 1.3 | 2.5 |
| Stdev | 9.2 | 5.4 | 0.3 | 0.4 | 1.2 | 3.1 |
| 95% confidence interval | 9% | 20% | 20% | 24% | 40% | 58% |
| | | | | | | |
| 4stroke S>1% | | | | | | |
| Number | 32 | 33 | 33 | 25 | 24 | 20 |
| Average | 63.1 | 29.5 | 1.5 | 1.7 | 2.9 | 6.0 |
| Stdev | 23.7 | 8.3 | 0.4 | 1.3 | 3.1 | 6.5 |
| 95% confidence interval | 13% | 10% | 10% | 32% | 44% | 49% |
| | | | | | | |
| **2-stroke engines** | | | | | | |
| Number | 33 | 35 | 35 | 30 | 28 | 25 |
| Average | 57.9 | 24.4 | 1.2 | 2.4 | 3.1 | 5.3 |
| Stdev | 35.7 | 17.7 | 0.9 | 1.6 | 2.2 | 3.3 |
| 95% confidence interval | 21% | 25% | 25% | 24% | 27% | 25% |
| | | | | | | |
| 2-stroke S<1% | | | | | | |
| Number | 14 | 15 | 15 | 11 | 11 | 10 |
| Average | 39.5 | 9.4 | 0.5 | 1.1 | 1.7 | 3.3 |
| Stdev | 18.1 | 5.3 | 0.3 | 0.6 | 1.7 | 2.4 |
| 95% confidence interval | 24% | 29% | 29% | 33% | 59% | 46% |
| | | | | | | |
| 2-stroke S>1% | | | | | | |
| Number | 20 | 21 | 21 | 20 | 18 | 16 |
| Average | 70.3 | 34.8 | 1.7 | 3.0 | 3.9 | 6.5 |
| Stdev | 39.0 | 15.3 | 0.8 | 1.5 | 2.1 | 3.1 |
| 95% confidence interval | 25% | 19% | 19% | 22% | 25% | 24% |

Figure 9 and Figure 10 show the emission factor of $NO_x$ as a function of sulphur content for 4-stroke engines and 2-stroke engines. A small increase of the emission factor with S content is observed.
There are three effects that may contribute to this phenomenon and explain the observation:
First is that slow speed engines, which generally have higher emission factors for NOx, are often using HFO. Therefore higher emissions of sulphur caused by HFO

are often accompanied with higher NOx-emissions caused by slow-speed engines. The attribution of ships as 4-stroke or 2-stroke may be biased.
The second explanation could be that HFO generally contains higher amounts of organic bound nitrogen which is completely converted to $NO_x$. This effect can increase the emission factor of $NO_x$ up to 15%.
A third effect is probably the correlation between S-content of fuel and the content of ashes and other precursors of aerosols in the fuel i.e. fuels with high S-content may have higher ash content which may lead to higher emissions of particulate matter.

Higher sulphur content is here probably related to the usage of fuels with higher content of ashes etc. The emission factors lie within the range of the EMS values (Table 6) that would lie between 60 kg/ton fuel for vessels from the years between 1990 and 2000 and around 40 kg/ton for newer vessels. A similar result is obtained for 2-stroke engines where EMS estimates would lie around 80 kg/ton fuel and 60 kg/ton fuel for the newer vessels and emission factors are found to be approximately 60 kg/ton. The emissions are not significantly different from those obtained for 4-stroke engines. This is also illustrated in Table 13.

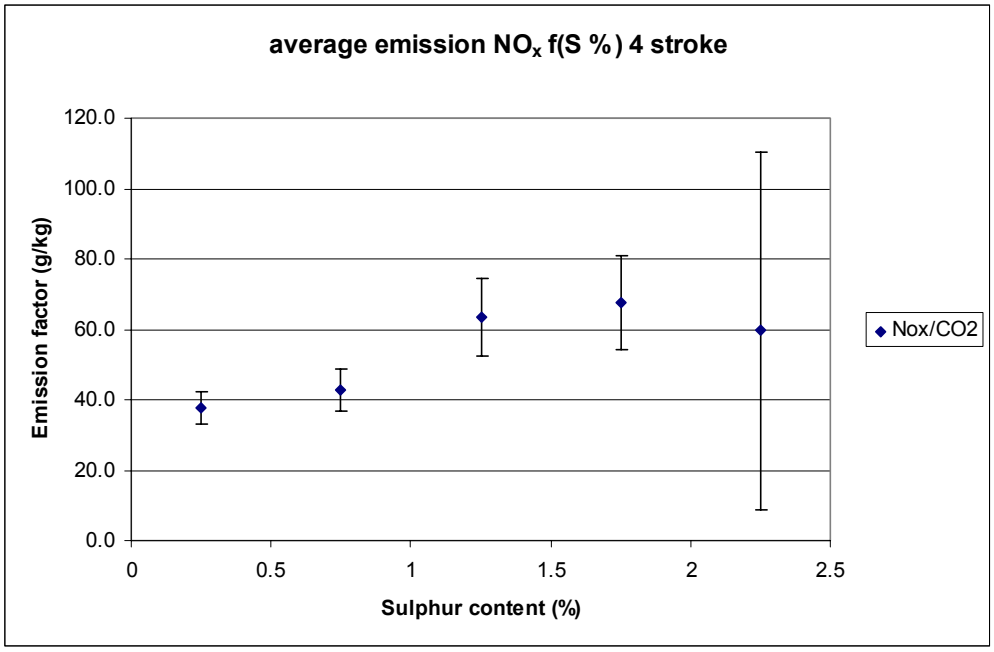


*Figure 9 The emission factor of $NO_x$ as a function of sulphur content for 4-stroke engines.*

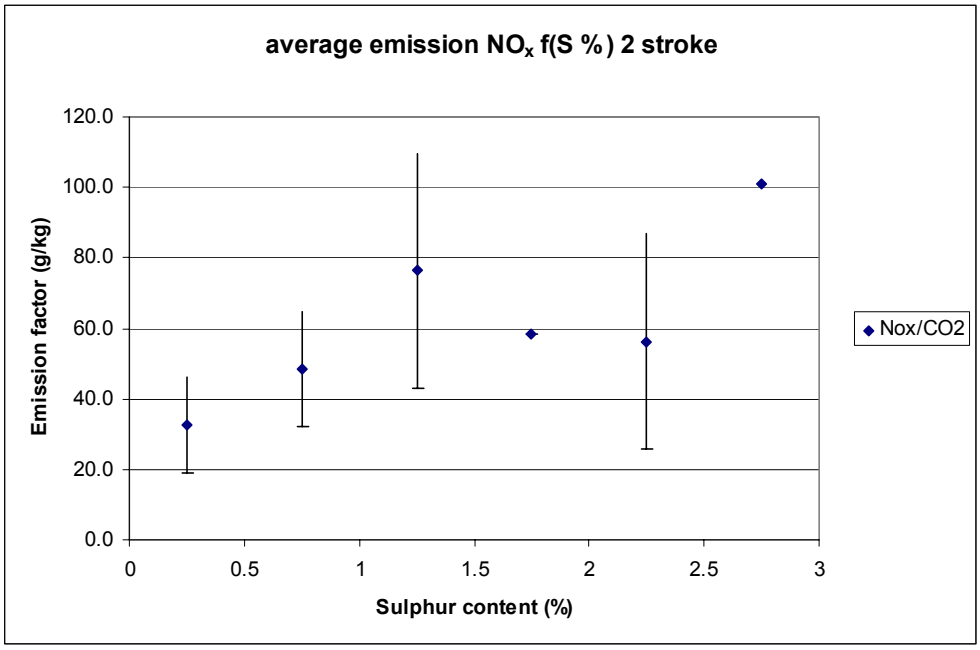


*Figure 10 The emission factor of $NO_x$ as a function of sulphur content for 2-stroke engines*

Figure 11 shows the emission factor of $NO_x$ as a function of age classes (see Table 14) for 4-stroke engines. No significant trend is observed. The decrease is also difficult to detect because of the small number of older ships in year class 2 to 4. It should be noted however that, according to Table 3 the fuel usage per kWh has decreased significantly by some 20% from 1974 to now. This means that if the emission per ton fuel remains equal, the actual emission factor per kWh will go down. The decrease in fuel usage is smaller however since 1990. For 2-stroke engines (illustrated in Figure 12) the situation is rather unclear due to the low number of measurements. There seems to be a maximum in the emission factor for $NO_x$ for vessels built in a second half of the 1980's . It is interesting to note that this trend is similar to the trend in EMS emission factors.

*Table 14 Building year classes.*

| Year class | Start of class | End of class |
|---|---|---|
| 2 | 1974 | 1979 |
| 3 | 1980 | 1984 |
| 4 | 1985 | 1989 |
| 5 | 1990 | 1994 |
| 6 | 1995 | 1999 |
| 7 | 2000 | 2006 |

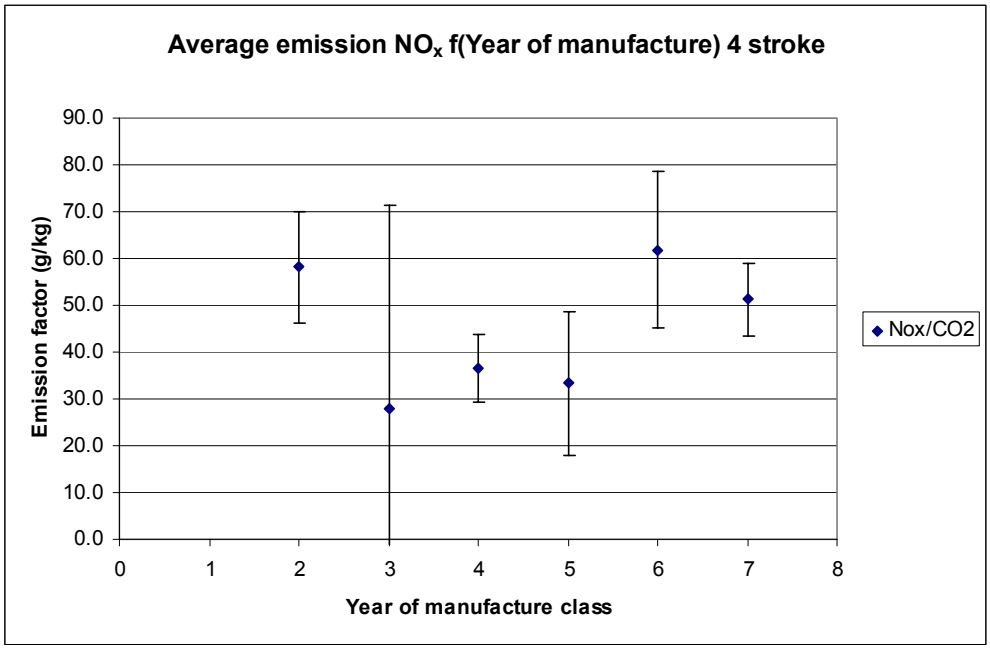


*Figure 11* *The emission factor of $NO_x$ as a function of building year class (I = etc.) for 4-stroke engines (95% confidence interval indicated).*

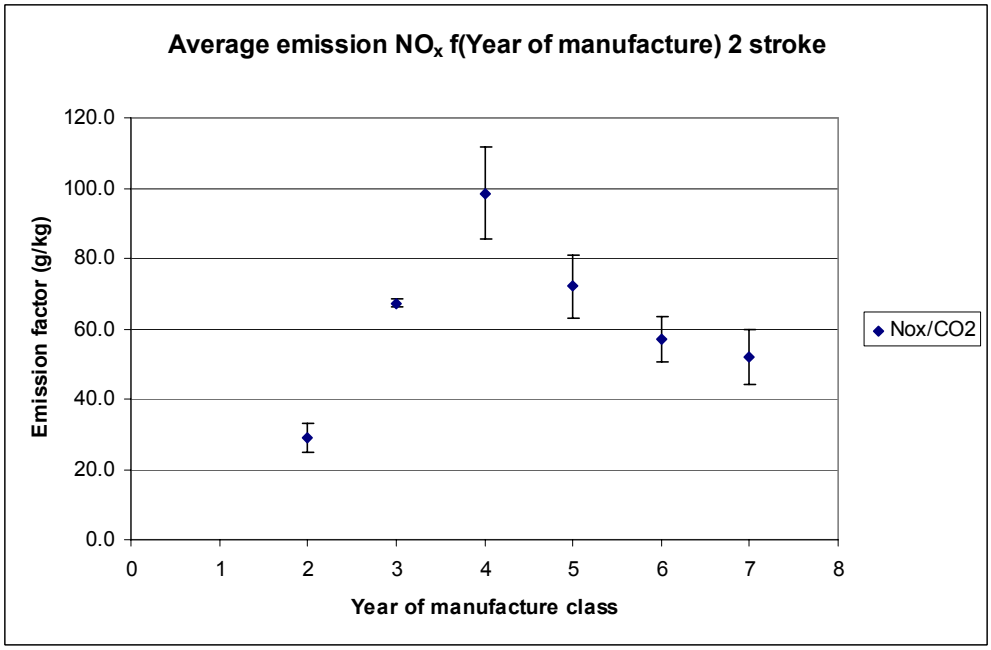


*Figure 12* *The emission factor of $NO_x$ as a function of building year class (I = etc.) for 2-stroke engines. (95% confidence interval indicated).*

## 4.3 Discussion on errors

Random and systematic errors are relevant here. With respect to the random error the following is important:

For $PM_{2.5}$ and $PM_{10}$:

- The uncertainty in the calculation of the emission factor is quite small. The $CO_2$ content of oil is fairly constant. The assumptions made to calculate $CO_2$ emission are rather certain and do not contribute to the random error.
- The variation (standard deviation) is around 100% of the mean. (see table 11).
- The total number of measurements is now around 100 after rejection of results with large errors. The overall average would therefore now have a 95% confidence interval of 20 %. Of course this number increases when specific classes of ships are selected. But this is at the same time done to decrease the variation.

For $NO_x$

- The variation (standard deviation) is approximately 50% of the mean. The overall average would therefore now have a 95% confidence interval of 11 %.

Estimating the systematic error in the result for particles is rather difficult. The processes contributing to the error:

A: Optical measurements of the particle size distribution. The uncertainty is estimated to be 40%.
B: Estimation of the particles density. The uncertainty is estimated to be 30%.

The total error in the product A*B can be calculated by summing the squared errors of the individual components (the square root of the variances) $\sigma_{tot} = \sqrt{\sigma_A^2 + \sigma_B^2}$

This leads to an uncertainty of some 50% for PM and 5% for $NO_x$. This would be the maximum error. As outlined above the uncertainty may decrease by the measurements of particle mass with a reference instrument (TEOM) and by the measurements with the cascade impactor. This should decrease the systematic error to a lower value for PM. The mass estimated with the LAS particle counter differed usually less then 20 % from the TEOM estimates. The maximum systematic error may therefore be less then 20 %. This seems a reasonable estimate for the systematic error in $PM_1$ emission factors. For $PM_{10}$ this could be an underestimation causing, for example, the lack of correlation with for example sulphur content of the fuel. The correlation with sulphur content present in the $PM_1$ emission estimates should also be present in the $PM_{10}$ (and $PM_{2.5}$) estimates. The fact that this is not observed suggests that there is considerable noise in the $PM_{10}$ estimates.

For $NO_x$ more information is available. In a different study carried out for the Port of Rotterdam quay side measurements were carried out at the same time as measurements on board of ships. The difference between the $NO_x$ emission estimated from funnel measurements and quay side measurements was on average less then 10 % in three measurement cycles (see Appendix 3). This shows that the quay side method can provide good quality result.

# 5. Discussion and conclusions

The goal of this study was to improve the quality of emission factors of $NO_x$ and PM by seagoing vessels. It was the aim to improve insight by doing actual measurements. Different methods to estimate such emissions were evaluated in the proposal phase and it was decided to evaluate different methods in the first phase. Three different cases were considered:

- emissions of ships at berth
- emissions of ships on the Netherlands continental shelf (NCP)
- emissions of ships sailing and manoeuvring in the Netherlands

## 5.1 First phase: Desk studies and test campaigns

In the first phase of the project possibilities to derive emissions from these three categories were evaluated. It proved impossible to derive accurate emission from measurements of $NO_x$ and PM from measurements carried out on the Dutch coast. There were two causes for that:
During winds from the North-West sector the contribution of emissions of $NO_x$ and $PM_{10}$ could hardly be distinguished from the contribution of sea spray. During winds from the South-West corner the background of emissions from the United Kingdom proved problematic. Therefore it was decided to pursue this idea not further. Other methods to measure emissions at sea were estimated to be very costly and were also discarded at this stage. It was suggested to derive emission factor for ships at the NCP from measurements carried out near the Dutch coast or in canals such as the Nieuwe Waterweg and correct for the difference in engine power between open sea and these canals, where appropriate.
Two campaigns were carried out in the first phase to investigate the possibility to measure emissions of ships at berth by a new plume method. It appeared that the method could be used but that the conditions required to carry out measurements were difficult to find. This problem was related to the fluctuating influence by plumes of other sources such as cars and other ships. It proved difficult to distinguish the plume from the ship that was the subject of the study and other plumes. Measurements were also hindered by large infrastructures such as buildings. Also in view of the rather detailed study that was carried out recently it was decided to not put extra effort in emissions of ships at berth.

## 5.2 Main phase: Field measurements

Most effort in the study was put in measurements of ships sailing in the Dutch territory. A new plume method was used to this purpose. The method appeared quite useful in studies of emissions by inland ships because many individual ships can be assessed in one working day. After some preliminary tests it appeared that it

was difficult to measure emissions of $PM_{10}$ with sufficient accuracy. The measurement strategy was changed to improve the situation and lower the possibility of large systematic errors in the results. This process severely hindered progress in the project. First the quality of the results is discussed.

*Statistical quality of the result*
By a combination of different monitors it seemed possible to estimate emissions of $PM_1$, $PM_{2.5}$ and $PM_{10}$ with a systematic error between 20 % and maximum of 50 %. The systematic errors in measurements of emissions of $NO_x$ are quite low as became clear from an independent study carried out in Rotterdam. This study and the results are described in Appendix 3. The measurements carried out in Rotterdam did not lead to conclusive results regarding the quality of measurements of particle emissions.
The variability of emission factors of PM and $NO_x$ of seagoing ships however is large, especially for PM. This is related to the large variation in, for example, engine types and fuel quality. This variation is much larger than in emission factors for inland ships. During the campaigns carried out in the study reported here some 150-180 vessels were investigated (depending on quality criteria the number of measurement used in the analyses varies from component to component). It appeared that the variation in emission factors of PM was nearly 100 % whereas it was only 50 % for $NO_x$. An overall average could, in principle, then have a statistical uncertainty of 15-20 % for $PM_{10}$ and 11 % for $NO_x$ (95% confidence interval). Table 14 shows the confidence intervals split for 4- and 2-stroke engines.

*Table 15 95 % confidence intervals for emission factors derived in this study.*

| | **$PM_1$** | **$PM_{2.5}$** | **$PM_{10}$** | **$NO_x$** |
|---|---|---|---|---|
| 4-stroke engines | 26% | 35% | 41% | 11% |
| 2-stroke engines | 24% | 27% | 25% | 21% |

*Representativity*
The sample that is taken from ships sailing into Dutch harbours is not by definition representative. Depending on several factors, such as location of the measurements etc. specific ship types may dominate the sample. Therefore it is important to stratify the data and derive emission factors for different groups. These emission factors for specific groups may then be used in the process of making estimates of emissions for entire fleet. The emission factors are then coupled with statistical data of fleet composition (for example the number of ships in a specific class) The number of ships that are measured in a specific class is then lower then the total number of course. But if the stratification is properly the variability in each group is also lower and the uncertainty in each group is also lower. Then only the uncertainty of the average in each group is important. This could be derived from the number of measurements in each class and the standard deviation of the average. Table 14 shows that the 95 % confidence intervals for the derived emission factors are not large. It may be concluded that statistical errors are not really important here. Sys-

tematic errors may be much more important. These include systematic errors in the measurements (described above) but also errors caused by non-representative sampling.
One of these is the representativity of the measurements for ships sailing at full speed. Little is known on the power used when sailing through the Nieuwe Waterweg for example. It makes sense to assume that outgoing vessels would be using a large fraction of their maximum power. Incoming ships may use less and may also use auxiliary engines running at high load. This could bias the result. The poll carried out (see Appendix 2) gives some idea. It appears that often ships use the same fuel for auxiliary engines and the main engine. The power of the main engine is much larger however. It seems therefore that bias because of the use of auxiliary engines could not be a problem. The poll results are not conclusive on the topic of the load used when passing our measurement site. Some vessels were at least running at more than half of their maximum speed. Specialists from the Port of Rotterdam authorities confirm that ships entering the harbour close to our measurement sites would run at 50 to 80 % of their maximum power. Outgoing ships will probably be running at even a higher load. Table 3 shows that the sensitivity of the emission factor to the load is rather small, even when the engine is running at 25 % of maximum load. We conclude therefore that the measurements could be quite representative for engines running at 50 to 100 % of their maximum load. This result suggests that the error introduced by low speed sailing could be less then 10 %.

*Generalized results*
There are two ways to look at the average results for emission factors. Both are discussed below.

1) Overall average emission factors
As a first approach overall average results of all measurements are presented in the small table below. In total six campaigns were carried out and the emission factors of some 180 vessels were measured. Some measurements were rejected in the QA/QC procedures. Especially PM measurements were rejected because of poor quality. This is usually caused by large fluctuations in background concentration and cannot be avoided. The averages given in the table are based upon 81 (for $PM_{10}$) to 128 (for $NO_x$) observations. Although the number of measurements is large compared to other studies it is still only a small sample of the ships entering the harbour (several tens of thousands per year). Contrary to our results for inland shipping the sample is not, as such, representative for all ships. One of the causes for this difference is that sea going vessels show a larger range of emission factors. This is related to the larger range in tonnage, engine power and type and fuel type. The observed average emission factor might be dominated by the smaller ships in the sample because these ships outnumber the larger ships. Consequently it is uncertain how representative these average results are for the large number of ships entering the port of Rotterdam. This problem is illustrated by the observation that averages observed differ for each sampling site because the fleet composition (in tonnage) passing the site differs (see table 12). With the larger vessels observed in

last two campaigns the emission factor for NOx is higher. The results are therefore difficult to compare with literature data and it is difficult to draw conclusions. Therefore a different approach to the data, in which more information on vessels in the sample, is more appropriate and discussed below.

| | PM1 | PM2.5 | PM10 | NOx1) |
|---|---|---|---|---|
| Overall averages | 1.7 | 2.6 | 4.7 | 50 |

2) Parameterised emission factors
In a second approach data are compared with earlier estimates presented in EMS. The relation between emission factor and several parameters that determine emission factors was investigated. This study was focused on the parameters used in the EMS study. To this purpose ships have to be classified according to classes used in EMS. These characteristics such as engine type and age and several parameters of each ship could be traced with the help of various sources (photographs, internet) and especially staff from the Port of Rotterdam.

In the Dutch emission registration and monitoring project (EMS) emission factors are used for $NO_x$ and $PM_{10}$. Emissions estimates of the fleet are based upon parameters such as the vessels age, fuel usage and engine type (as illustrated in $2.2) The possibilities for comparison differ for $NO_x$ and $PM_{10}$. Since more information on $NO_x$ emission factors is available the parameterisation is more detailed and complex than it is for $PM_{10}$. As a result the figures reported in EMS cannot always be easily compared with our results for $NO_x$ in all cases.

Our limited dataset does not allow rigorous statistical analysis and investigate the dependency on all parameters used in EMS. The number of good quality data in the set was decreased further because not all information of each vessel could be obtained. Some forty vessels could not be traced reducing the number of vessels in each category further and statistically reliable results could not be obtained for all categories. Table 16 provides an overview which is discussed below:

Categories that could be investigated are:

1) Age of vessel
On average the studied vessels were built between 1995 and 2000. The correlation between the age of the vessel and the emission was investigated and the following conclusions were drawn from the results:

- There is hardly a correlation observable between the emission factor for PM and the age of the vessel. In EMS only a weak correlation is assumed.
- The measured emission factor for $NO_x$ in general varies only to a limited extent with age of the vessel. It is interesting to see how the emission factor for 2-stroke engines shows a maximum for vessels built in the 1980's. This is strikingly similar to EMS estimates.

2) Fuel type
Contrary to EMS no difference was made between the use of MDO or HFO. One reason for that was the quality of this assessment (whether a vessel uses MDO or HFO) that was sometimes poor. Only for nearly 100 vessels an assessment of the fuel type that was used, could be found. Moreover it was considered that the sulphur content derived from measurements of the emission factor for sulphur dioxide was a good proxy.[5)]

It is striking to observe that the above average emission factor for NOx for all vessels is lower then the parameterised averages. This must be related to the fact that many of the vessels of which the engine type etc could not be classified have smaller NOx emission factors. This could understood if it is realised that the many of the unidentified ships belong to the smaller category. These smaller vessels are more difficult to identify and classify.

In an attempt to improve the statistics of the results all data were pooled and the emission factor for PM was compared with S content. This has the advantage that the lack of information on engine type or fuel usage is not a problem. This result is shown in Appendix 4. It appears that quite a good correlation exists between $PM_{10}$, $PM_{2.5}$ and especially $PM_1$ emission factors and sulphur content of the fuel. The results do not differ very much from the un-pooled results. It was concluded that there is a significant correlation between the emission factor of PM and sulphur content of the fuel. This is especially the case for $PM_1$. The sulphur content was derived from measurements of the emission factor of sulphur dioxide. It should be noted that it is, in principle, unclear what causes this relationship. Literature data however show that S-content is an important factor for emissions of particulate matter (see also Duyzer *et al*., 2006). This can be understood quite well from our knowledge of sulphur oxidation in the engine. Therefore it is concluded that S-content is indeed an important parameter for the emission of particulate matter and that the results of our study may be used to quantify this relationship.

5 After the presentation of earlier versions of this report the quality of the assessment of S emission factors was discussed. Therefore considerable effort was put into the quality of the measurements of S emission factors. This subject is discussed in Appendix 2. It was concluded that the S emission factors derived for MDO user were quite close to what could be expected. The emission factor measured for HDO users was rather low. The underestimation could be 25 % as a maximum. This difference could at the same time be caused by the wrong assessment of vessels as HDO or MDO users. At this stage it was considered that the emission factors for sulphur could very well be correct.

*Table 16 Emission factors of PM and $NO_x$ in g/kg derived from this study and EMS.*

| | This study | | | | EMS | | |
|---|---|---|---|---|---|---|---|
| **4-stroke Engines** | **$PM_1$** | **$PM_{2.5}$** | **$PM_{10}$** | **NOx[1)]** | | **$PM_{10}$** | **$NO_x$[2)]** |
| S<1% | 0.8 | 1.3 | 2.5 | 39-63 | MDO | 1.6 (1.6-2.6) | 59 (42-82) |
| S>1% | 1.7 | 2.9 | 6.0 | | HFO | 3.9 (3.6-4.2) | |
| 2-stroke engines | | | | | | | |
| S<1% | 1.1 | 1.7 | 3.3 | 39-70 | MDO | 1.8 (1.8-2.8) | 88 (76-111) |
| S>1% | 3.0 | 3.9 | 6.5 | | HFO | 8.8 (8.1-9.7) | |

1) Averages observed in this study

2) Emission factor used in EMS for the period between 1995 and 2000. Emission factors for different years between 1974 and 2000 and thereafter are given between brackets.

In the table the range of emission factors used in EMS for ships built in the period, 1974 to 2000 and thereafter, are given. In addition the emission for vessels in the period 1995 to 2000 are given. These may be compared to the measured emission factors It was already noted that it was difficult to obtain good quality data for engine type for all vessels. Therefore the attribution of each ship to a specific class is sometimes uncertain and many ships could not be used for this analysis. To which uncertainty in the result this leads is presented elsewhere in the report (table 12). Another problem is the distinction between MDO and HDO which is also uncertain.

As an example: the emissions of seagoing vessels will be dominated by two stroke engines using HFO. The emission factor in table 15 represents this number. Our emission factor for 2-stroke engines is split up in two classes (one with S content below 1% and one with a higher S content). The category with S content above 1 % (with an emission factor of 70 g/kg) is probably more representative for the EMS estimate for slow speed, HFO using, engines (88 g/kg). The EMS estimate is based upon information of all vessels using information on engine type, vessels age and fuel type. The difference between the EMS estimate and the result of this study is nearly significant at the 95% interval.
Similar discussions may be held for 4-stroke engines. Here the distribution across classes is not so simple. Both HFO and MDO are used. The results of our limited sample of 4-stroke engines is probably not exactly representative for the same

group of ships used to estimate the emission factor in EMS. It should also be noted that the difference information supporting the EMS estimates for NOx is large. For PM the situation is simpler. The emission factors are given in EMS only for two classes and are (only little) depending on the vessels age. In view of the average age of the ships in this study the emission factor could be rather similar. In this case therefore the comparison between EMS estimate and the result of this study is more valid. In view of the uncertainty in the derived average numbers there are hardly significant differences (95 % confidence level) between emission factors of $PM_{10}$ used in EMS and found in this study. Only the emission factor for $PM_{10}$ is significantly lower then the one assumed for HFO-using 2-stroke engines (8.8 g/kg). It should be noted that this is an important category. At the same time the uncertainty in the EMS estimates for this category is comparatively high (private communication Jan Hulskotte, TNO)

To make an exact comparison between the results presented here and the EMS estimates would require a specific recalculation of the EMS figures. This could be done in a latter stage by the authorities responsible for EMS estimates (Task force on Traffic and Transport of the Dutch Emission Registry)

*Consequences and recommendation*
As was outlined above it is difficult to draw conclusions and recommend the usage of the overall results of this study for NOx in the Dutch emission assessment protocol. Large differences between the emission factors reported here and EMS estimates for different classes were not found. It should be noted that the EMS estimates are based on a rather large volume of literature material for $NO_x$. The emission factors estimated in this study do not differ significantly from EMS estimates. This fits well with the goal of this study to improve insight into the (quality of) emission factors for NOx. At this stage therefore it is not recommended to change current estimates for NOx.
The emission factor for PM differs more strongly whereas at the same time emission factors in EMS are not so well based as the factors for $NO_x$. Especially the emission factor used in EMS for 2-stroke engines using HFO is rather uncertain and could be biased. It is therefore recommend to lower these estimates to values observed in this study and to use the dependency of S-content as observed here.

In Appendix 5 a preliminary attempt is made to estimate the impact of the results of this study on estimates of emissions of PM by shipping in the Netherlands. Based on the above, emissions of $NO_x$ were not changed.
Based on this study an emission factor of 6.5 g/kg was used to estimate emissions by shipping for the Dutch continental shelf, ships at berth in Dutch territorial waters and for ships sailing in Dutch inland waters. For all categories the emission would go down by 20 to 25 %.

The effect of SECA guidelines maximizing the sulphur content of fuel at 1.5 % was also calculated. Here a linear proportion between PM emissions and sulphur content was assumed. The proportionally was derived from the observed correlation between S content of the fuel and $PM_1$ emission factors. The effect of introducing this SECA rules would lead to a reduction of the PM emission with 10% for all three source categories.

**Acknowledgments**
The support by Ron van Gelder from the Port of Rotterdam is gratefully acknowledged here. Ron was a great help in finding data on ships characteristics. The help of the DCMR staff is also acknowledged. They provided an additional TEOM during one of the campaigns and made measurement data from the DCMR network available.

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# 7. Authentication

Name and address of the principal:

Ministry of Transport Public Works and Water Management
The Netherlands

Names and functions of the cooperators:

| | | |
|---|---|---|
| Jan Duyzer | - | TNO |
| Koos Hollander | - | TNO |
| Marita Voogt | - | TNO |
| Henk Verhagen | - | TNO |
| Hilbrand Weststrate | - | TNO |
| Rob Schimmel | - | TNO |

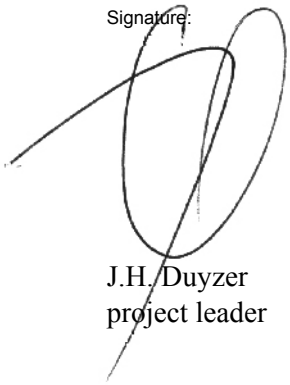
Names and establishments to which part of the research was put out to contract:

| | | |
|---|---|---|
| Arjan Hensen | - | ECN |
| Aline Kraai | - | ECN |
| Gerard Kos | - | ECN |

Date upon which, or period in which, the research took place:

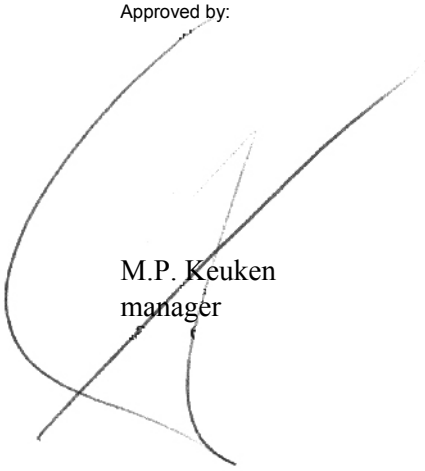
January 2006 – March 2007

Signature:



J.H. Duyzer
project leader

Approved by:



M.P. Keuken
manager

# Appendix 1 Monitoring instrumentation

All measurements have been carried out using a mobile system, consisting of a small truck, in which the instruments are transported and operated. This allows carrying out measurements at various locations, moving fast from one to the other, but also to carry out measurements while driving. The instrumentation in the van is described below.

**$CO_2$/$H_2O$ analyzer**
The Li-6262 is a differential, non dispersive infra red (NDIR) analyzer produced by LI-COR. The quantification of $CO_2$ and $H_2O$ is based on the difference in absorption of infra red radiation in a sample cell, through which the sample to be measured is drawn and reference cells for respectively $CO_2$ and $H_2O$. The reference cells contain $CO_2$ and $H_2O$ in known concentrations.

**$NO_x$ analyzer**
The CLD 700 AL is a chemiluminescence NO-$NO_2$-$NO_x$ analyzer produced by Eco-Physics. The range of the instrument is 0-100 ppm.
This analyzer is equipped with two channels and two separate reaction chambers, allowing simultaneous measurement of NO and $NO_x$. $NO_x$ is the sum of NO and $NO_2$. The latter is thus obtained by difference of $NO_x$ and NO.

NO reacts with ozone ($O_3$) generated in the instrument:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6)$$

Part of the $NO_2$ is formed in an electronically excited state, decaying back to the ground state, emitting the characteristic chemiluminescent radiation, the intensity of which is proportional to the original NO concentration and measured by a photomultiplier tube.
To measure $NO_2$ it has to be reduced to NO, for which a thermal (molybdenum, Mo) converter is used:

$$3\,NO_2 + Mo \rightarrow 3\,NO + MoO_3 \qquad (7)$$

**Condensation particle counter**
The condensation particle counter (TSI model 3022A) measures the number of particles continuously in the stream of air drawn through the instrument. In order to detect the particles isobutanol is condensed on the particles to bring them in the detectable size. Particles with diameters above 10 nm are detected with a measurement range from as low as 0.007 particles per $cm^3$ up to 9.99 $x10^6$ particles per $cm^3$.

**Aerosol Spectrometer**

The Laser Aerosol Spectrometer (LAS-x) counts the number of particles while classifying them in 16 different diameter classes.
Assuming spherical particles and particle densities taken from literature (varying from 1 to 1.6 g/cm$^3$) the number particle distribution is first recalculated to volume distribution and then to mass distribution. By comparing the average volume distribution over one day with the slow mass measurement (see TEOM), a proper adjustment of the particle density is obtained.
The instrument, allowing a time resolution of 1 second, was instead used with 10 seconds time resolution, which reduces the noise in the calculated mass.
In the calculation of the emission factor, the PM as well as the $CO_2$ concentration is integrated over the passage time of the plume, typical 30-80 seconds. Therefore the lower time resolution is not a limiting factor, regarding the validity of the result.

**Laser range finder**

A Leica, type LRF 1200 laser distance monitor is used to measure the distance to the ships. The instrument is able to measure distances up to 1200 m, with an accuracy of one meter.

**TEOM dust monitor**

The measurement principle of the TEOM (model 1400) is based on the relation between the vibration frequency of an oscillating body and its mass (Tapered Element Oscillating Microbalans).
Air is drawn through a filter which collects the particulates. The filter is coupled to the oscillating body. The vibration frequency changes with increasing mass load on the filter. The vibration frequency is continuously measured together with the air flow rate through the filter, from which the concentration is derived.
The sampled PM fraction ($PM_{10}$, $PM_{2.5}$ or even $PM_{1.0}$) is defined by a size selective inlet.
The calibration is based on the fundamental physical relationship between mass and vibration frequency. This is expressed by the unique value of the spring constant which is determined by the manufacturer of the instrument.
To obtain a stable output signal, filter and air drawn through it are heated and temperature controlled. As a result of the heating there will be a loss of volatile particulates. To compensate for this loss a correction factor (EU recommendation) of 1.33 is applied to the measured results to bring these in agreement with the EU reference method.
The FDMS (Filter Dynamics Measurement System) version of the classical (model 1400) TEOM, automatically compensates for this loss of volatile material. The above mentioned correction is avoided with this version. DCMR uses a SES (Sample Equilibrium System) version, which is the intermediate option of the Classical TEOM 1400 and FDMS 8500 version.

**Osiris dust monitor**

The measurement principle of the Osiris is based on forward light (0.67 μm) diffraction by dust particles in the air drawn through the instrument. Each particle passing through the measurement cell is illuminated by a laser and gives a pulse of diffracted light to the detector. The height of the pulse is a measure of the particle size. Thus, the mass of each particle is determined. Counted mass is registered, classified according to size. From this data various mass fractions can be calculated ($PM_{total}$, $PM_{10}$, $PM_{2.5}$ or $PM_{1.0}$) and displayed.
The air inlet of the Osiris is heated to avoid the entrance of water droplets or particles significantly increased in size by condensation of water on them.
The mass concentration is calibrated by comparison with reference or reference equivalent mass monitors.
The measured particle size is limited at the lower diameter side by the wavelength of the laser light (lower diameter limit 0.5 μm) and at the upper diameter size by the inlet geometry (upper diameter limit 20 μm).

**GRIMM dust monitor**

The measurement principle of the Grimm (model 1.108) is similar to that of the Osiris. The geometry of the measurement cell is however different: 90° light scattering.
Particles with diameters between 0.30 and 20 μm are counted and size classified in 15 channels, from which the mass distribution is calculated with the help of a calibration factor.
In its standard version (model 1.108) it does not have any heating at the inlet.
The mass concentration is calibrated by comparison with reference or reference equivalent mass monitors.

**Cascade impactor**

The measurement principle is based on inertial impaction. The sampler consists of a pile of plates with slits decreasing in size with each plate in the pile. The slits are shifted horizontally with respect to each other. The plates are covered with a filter. Sample air drawn over these plates is forced to bend over the plates with increasing velocity when the slits become narrower and thus particles impact on the various plates due to their inertia which is related to particle size and mass. Thus particles are separated in various size fractions.
The mass on the various plates is determined by weighing.

**ELPI**

The electrical Low Pressure Impactor combines the accuracy of the size classification of an inertial impactor with the fast and sensitive measurement of the particle charge as a measure of the deposited mass on the various stages of the impactor. Sampled particles are charged in the inlet section of the ELPI and than separated according to size in the cascade impactor section. The measurement of the electrical charge allows fast and continuously monitoring of the number of particles

deposited on the various stages of the impactor. The ELPI measures the number particle size distribution of particles between 30 nm and 10 μm.

**$SO_2$ analyzer**

The Thermo Electron Model 43 A $SO_2$ analyzer is based on the principle of pulsed fluorescence. Air is continuously drawn through the analyzer and irradiated with pulsed UV light in the measurement cell. $SO_2$ molecules in the cell are excited to a higher energy state and than decay back to the ground state producing fluorescent light. This fluorescent radiation which is proportional to the concentration of $SO_2$ in the air is measured continuously.

The detection limit is 1 ppb, at a response time of one minute. The noise is than about 0.5 ppb and the precision 1 ppb.

We made the instrument faster by decreasing the response time though an increase of the flowrate.

# Appendix 2 Analyses of measurements of emissions of vessels that were part of the poll by the port of Rotterdam authorities

## Introduction

The sulphur emission estimated from the plume measurements was used to estimate the S content of the fuel used during passage. The assumption was made that 1 % S in the fuel leads to an emission of 20 g sulphur dioxide per kg fuel. From this figure and the emission calculated from the plume measurements, the sulphur content in the fuel the ship was using during passage of the measurement site was calculated.

## Results

The results of these measurements are shown in Figure 13. The sulphur content observed for vessels classified as HFO users shows a maximum around 1.7 % S whereas vessels classified as MDO users show a maximum at 0.5 % S.
It is interesting to compare these results with other data.
A few vessels that passed our monitoring site were visited by the Port of Rotterdam authorities. The visit took place on the same day. The responsible officer (often Chief Engineer) was interviewed (on a voluntary basis) on several aspects of the vessels engine characteristics, fuel usage, its power usage during passage of the monitoring site especially. Similar questions addressed the presence and use of auxiliary engines. Our specific interest was the fuel composition with respect to sulphur.
Few ships were equipped with soot dust filtering. One with a Humid Air motor.

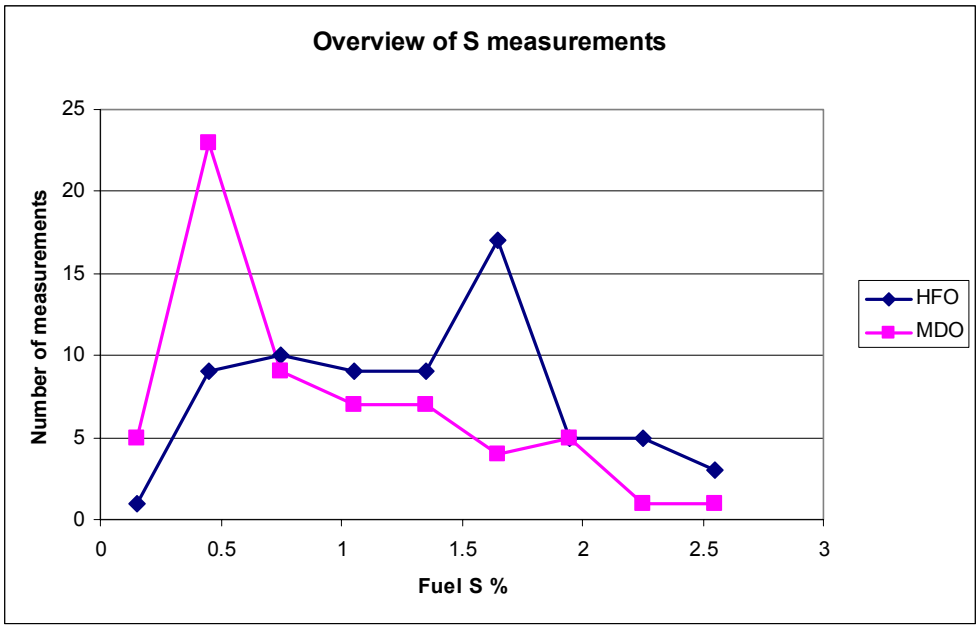



*Figure 13 Overview of results of measurements. The sulphur content of the fuel derived from the emission factor for ships considered either HFO users and MDO users.*

The result of our shoreline measurements were compared with the results of the poll. Figure 14 shows the results of this comparison. Estimates errors in the measurements results are indicated. Especially the lower estimates have large errors. This is often caused by uncertainty in the measurements in the $CO_2$ concentration. It should be noted that the figures given by the ships crew are *maximum* values for the sulphur content. This is because the quality of the fuel is characterised by the *maximum* sulphur content. The plume measurements are lower than the figures provided by the crew. It is difficult to judge these results. It could mean that the emission factors observed in this study are an underestimation, at least for sulphur. There are good arguments to assume that all sulphur present in the fuel will end up as $SO_2$ in the plume (although field measurements have often shown this kind of results.This result was investigated extensively:

- *Are the measurements correct?*
    - The calibration of the monitors was checked several times. This was done before and after the campaigns. The monitor appeared to be very stable. From literature information it was also concluded that the monitor would not be sensitive to bias caused by low temperatures (Uiterwijk *et al*., (1985)
    - All individual plumes were re-analysed using an improved procedure. In the reanalyses an estimate of the error in each individual plume was estimated.
    - The response time of the $SO_2$ monitor was checked and the influence of this response time on the determination of $SO_2$ peak in the plume was theoretically evaluated (Segers an Duyzer, 2007). It appeared that this effect was only marginal.
- *Is this result really unexpected?*
    - All literature seems conclusive with respect to the emission of $SO_2$ from S in the fuel and the S-content of the fuel used. Nearly all sulphur will end up as $SO_2$ in the ships plume. Only a few percent of the total amount of sulphur will end up in the particulate mode.
    - Conversion of the emitted $SO_2$ to particulate sulphur could, in principle, take place during passage of the ships plume from the vessels funnel to the monitor. This however could not lead to this large underestimation of a factor of two. If all emitted particles (usually less than 10 g/ kg fuel) would have been pure sulphur, it would still not explain the large underestimation of several tens of grams sulphur /kg.
- *Are assumptions about S content of the fuel correct?*
    - Several experts were consulted. These all responded that there is no reason to assume that the S- content of the fuel as mentioned by the ships officers would wrong. There is no reason for them mention a sulphur content higher then the real content. On the other hand the estimates are always a maximum and the concentration of sulphur in the fuels was not measured.
    - Results of other investigations into the sulphur content of the fuel were analysed. The Inspectorate of the Ministry of the Environment and Dutch customs also analyse sulphur content of fuels on a systematic a basis. They reported for 2003 S% ranging from 0.58

% to 3.63 % for HFO with an average of approximately 2.3 % and 0.74 to 1.6 for MDO users with an average of approximately 1.1 %. In 2005 the numbers for HFO were similar and a lower average for MDO users of 0.6% This shows that the percentages mentioned by the crew would be significantly higher than the actual sulphur content of the fuel used. And close to the percentages derived from our measurements

None of these activities leads to a conclusion that would explain the underestimation of the S content. On the other hand the results of measurements of actual sulphur content by customs and the inspectorate compare quite well with our results for *MDO.* Sulphur contents of the fuel are quite similar to our measurements displayed in Figure 13. Only for HFO our results could be an underestimation. Possibly HFO quality is improving with respect to sulphur or our classification HFO/MDO is not always correct.
At this stage we conclude that the results for MDO are correct and that the results for HFO are low by perhaps a maximum of 0.5 % compared to expectations on sulphur content. This could be caused by losses of sulphur in the vessels funnel or by the fact that the S content in the fuel is actually lower than expected. The latter cause could also be linked to the classification of the ships as users of HFO

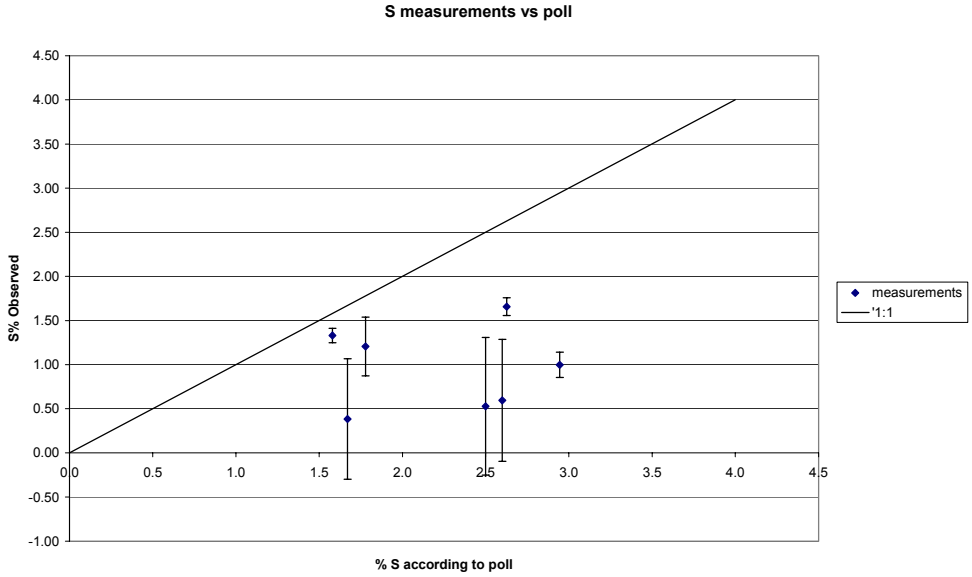



*Figure 14 The estimated sulphur content of ships fuel derived from measurements on shore compared to the information on the fuel content from the poll described in the text*

# Appendix 3 Measurement of $NO_x$ emissions in the Rotterdam harbour

In an independent research project carried out for the Port of Rotterdam estimates of the emissions were made using the method used in this project. The measurements were carried simultaneously with stack measurements carried out on board the ship.
During half an hour the vessel passed the monitoring site seven times. The emission factor calculated as the average of the 7 passes and the measurements carried out on board the vessel were compared. The results are displayed in Table 17. The measurements were carried out by different loads. On average the estimates differ by less then 10 %. This result suggests that the method can provide good results.

*Table 17 Emissions of $NO_x$ measured on board the ship and on the shore. All estimates in g/kwhr. The efficiency of the engine was determined during operation.*

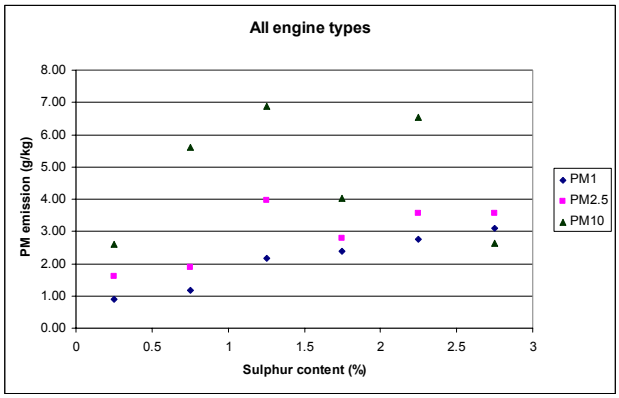
| On board measurements | Shoreline measurements |
|---|---|
| 12.05 | 11.26 |
| 12.88 | 12.89 |
| 12.27 | 10.72 |

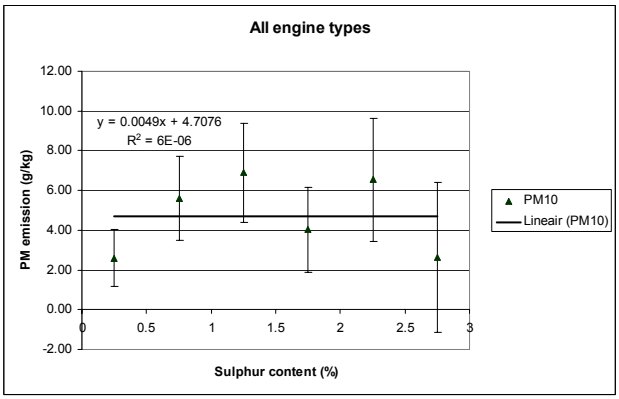
# Appendix 4 PM emissions as a function of S-content

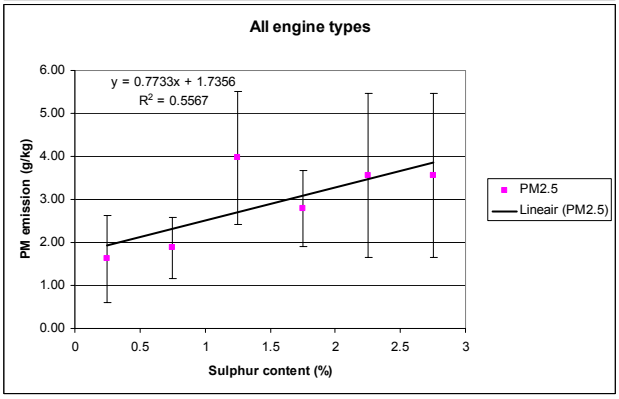
The results for PM show considerable scatter. In an attempt to reduce the scatter all emission measurements were treated together and plotted against the sulphur content of the fuel as derived from the measurements in the plume. The result is shown in Figure 15. It has improved compared to the individual results for 4 and 2-stroke engines shown above.

The $PM_1$ results are optimal showing a strong correlation between the emission factor and the sulphur content. For $PM_{2.5}$ the result contains more scatter and for $PM_{10}$ the effect is rather limited and not significant. It appears that the relation between PM emissions and sulphur content is lost in the scatter of the $PM_{10}$ emission factors.

In order to improve the statistical quality of the regression analyses only sulphur data with an uncertainty (standard deviation) of 50 % were used.



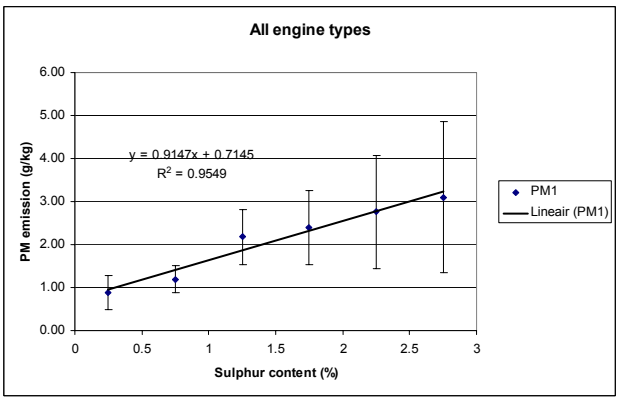




*Figure 15 Emission factors of PM as a function of sulphur content. In the top panel all size classes plotted together the lower panes give individual results with 95% confidence interval error bars.*

# Appendix 5 Estimates of the effect of new emission factors on emissions

It is interesting to investigate what the impact of new emission factors would be on the emission of PM in specific areas. At this stage when the emission factors observed in this project have not been accepted by the Dutch Emission registration it is necessarily only a first impression. At the same time it is interesting to observe what the impact would be of SECA guidelines regulating maximum sulphur concentrations in fuel.
To study this effect we have made new calculations of emissions by ships sailing on the Dutch continental shelf and Dutch inland waters. These are compared with original estimates and additional calculations showing the impact of SECA regulations. Current estimates are derived from the formal Dutch Emission database (2007)
A new emission factor of 6.5 g/kg HFO was used rather than the original estimate of nearly 9 g/kg (see $2.2) Figure 16 shows the effect of this change. Emissions for 2004 will decrease by some 25 %.
The effect of SECA rules were derived from the influence of sulphur content on emission factors. The results of the current study were used to this purpose. Especially the effect of S content on $PM_1$ emissions seems rather well established as was shown in $4.2 and Appendix 4. It is assumed that the effect of sulphur is only present in emissions of small particles. The emission of larger particles is probably not related to S content of the fuel and is therefore not taken into account (and not well established in this study) It is assumed that the emission of PM is proportional to the S content according to the figures below. Starting with a default emission of 4 g/kg fuel it is increasing directly proportional to the sulphur content.[1)]

Figure 16 shows that implementation of SECA rules will lead to a decrease of the PM emissions by roughly 10 %. Similar results are observed for emissions by ships sailing and manoeuvring in Dutch territorial waters (Figure 18) and slightly smaller effects are observed for ships at berth in Dutch territorial waters. The effect of the new emission factor on the latter emissions is nearly 22 % and the effect of SECA is nearly 9 % for ships sailing on Dutch waters (Figure 17).

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1) In a first crude approximation the following equation was used
EF_PM = S*X + B (g/kg fuel)
in which:
S = l% Sulphur
X= 1 (proportionality factor derived from measurements)
B= 4 (not exactly determined offset. In this case 4 g/kg was used a being representative for 4 stroke engines

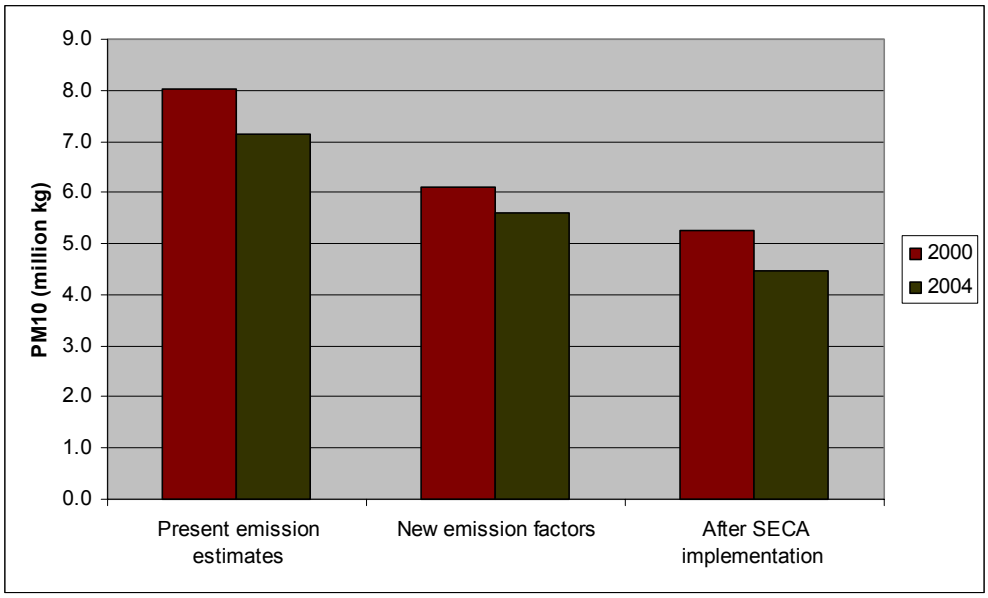


*Figure 16* *Effects of using new emission factors and SECA upon ships $PM_{10}$ emissions from the Dutch continental shelf.*

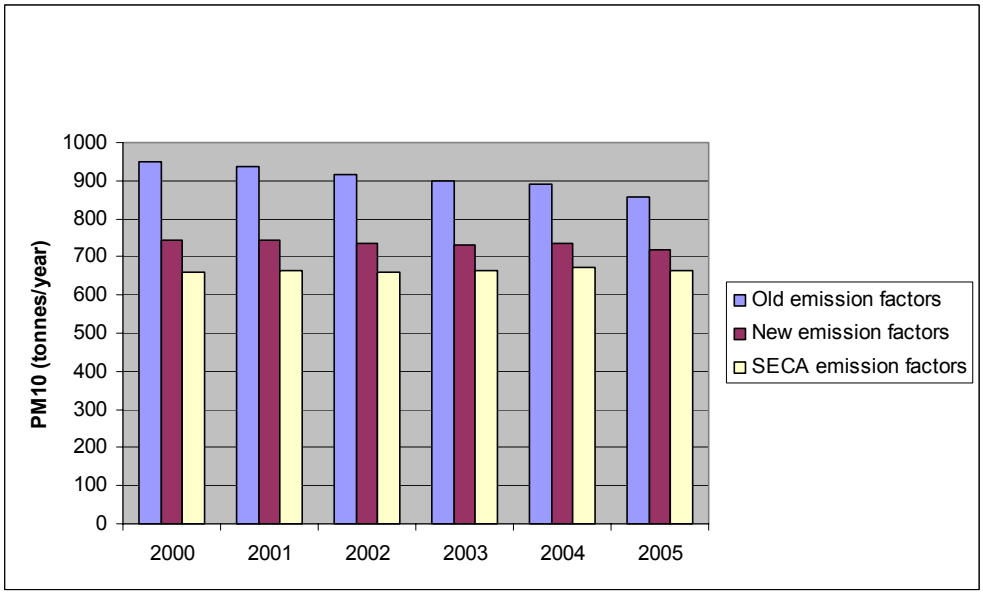


*Figure 17* *Emissions of sea going vessels manoeuvring and sailing on Dutch territorial waters.*

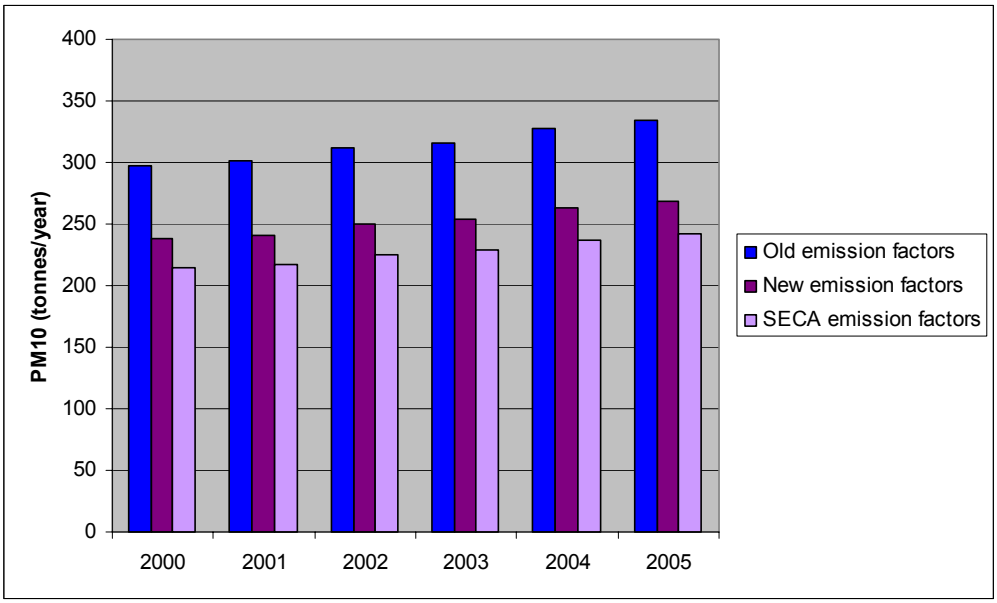


*Figure 18 Emissions of ships at berth in Dutch territorial waters*