TNO Environment, Energy and Process Innovation

FINAL REPORT

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TNO-report

R 97/435

Development and demonstration of a method
to monitor the effects of measures to reduce
VOC emissions in the EU.
LIFE 95/NL/A11/NL/365/ZHL [1966-1998]
(Final Report)

Date	January 1998
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Order no.	53397
Keywords	- VOC monitoring strategy - modelling - industrial area - Rijnmond-the Netherlands
Intended for	Mr. C. Pleinveaux, European Commission DG XI.B2

Project Characteristics	Description
Name	Development and demonstration of a method to monitor the effects of measures to reduce VOC emissions in the EU
Location	Rijnmond area, Rotterdam, the Netherlands
Contractor	TNO, the Netherlands
Duration	1/1/1996 - 1/2/1998
Objectives	To develop and demonstrate a methodology to assess VOC emissions, and to estimate the contributions by various source categories in a complex industrial area based upon ground level VOC measurements.
Activities	Phase I: 1/1/1996-1/4/1997 1) to develop a modelling methodology; 2) to select a measuring strategy; and 3) to consult national and international experts. Phase II: 1/4/1997-1/2/1998 1) to implement the measuring strategy; 2) to process the data in accordance with the modelling methodology; and 3) to report the outcome of the project.
Results	• demonstration of the methodology at Rijnmond, Rotterdam; • description and dissemination of the methodology.
Project costs *1000	ECU 430,- (NLG. 897,-)
Life contribution * 1000	ECU 209,- (NLG. 436,-) NLG. 375,- staffing; NLG. 15,- travelling; NLG. 18,- equipment; NLG. 14,- operational; NLG. 8,- dissemination/reporting; NLG. 6,- contingencies;
VROM contribution * 1000	NLG. 250,-
SHELL contribution * 1000	NLG. 100,- (in kind)
DCMR contribution * 1000	NLG. 100,- (in kind)

Executive summary

In 1996, TNO was granted by the European Commission to carry out in the framework of the LIFE programme a project entitled "Development and demonstration of a method to monitor the effects of measures to reduce VOC emissions in the EU". An additional grant was supplied by the Dutch Ministry for Housing, Physical Planning and the Environment. Two other organisations also contributed to the project: Shell Research Ltd., the Netherlands and the Environmental Protection Agency of Rijnmond (DCMR).

background

Ambient air concentrations of Volatile Organic Compounds (VOC) may cause health effects either directly by toxic compounds such as benzene and/or indirectly by formation of ground-level ozone. Next to traffic, industrial activities (i.e. chemical base, storage tanks and refineries) are important sources of VOC emissions. In order to implement cost-effective emission-reduction measures and to monitor the impact of these measures, information is required on stack and diffuse emissions of industrial areas.

project goal

In the Netherlands, the National Emission Inventory (EI) is used to collect information on VOC emissions. Subsequently, in combination with dispersion models, ground-level air concentrations of VOC are computed around industrial areas. The main constraints to apply this methodology are *firstly*, discrepancies with measurements of ground-level air concentrations, *secondly*; air concentrations estimated from EI data concern *annual* average concentrations and hence, there is considerable delay to provide this information and no information is available on fluctuations within a year for example during a smog-episode, and *thirdly*; EI data do not exist in all European countries. In order to address these constraints, *the goal of the project is to develop an alternative method to assess VOC emissions from industrial areas.*

project objectives

The objectives of the project are: i.) to develop a methodology to assess VOC emissions from complex industrial areas based upon VOC ground-level measurements and ii.) to demonstrate the methodology in the Rijnmond area by identification of various sources of VOC emissions and computation of the strength of the emission rates.

project methodology

After development of the measuring and modelling strategy and selection of a representative industrial area within the Rijnmond region, a measuring campaign has been implemented for a three month period. Subsequently, the measurement results have been used for model calculations of the emission rates and

compared with values of the National Emission Inventory. Finally, a method is recommended to assess VOC emissions from complex industrial areas.

In order to develop a methodology, two types of ground-level measurements of VOC have been tested: *within* and *outside* an industrial area. For "C_6 - C_8" hydrocarbons, passive samplers with a sampling period of two weeks have been applied, while for "C_2-C_5" and "C_6-C_8" hydrocarbons hourly on-line measurements and active sampling have been performed. Passive sampling is cost-effective and provides information especially on *spatial* variation of ground-level air concentrations *within* an industrial area. On-line measurements and active sampling are more costly and provides information especially on *temporal* variation of ground-level air concentrations up- and down-wind *outside* an industrial area. In addition to these rather traditional measurement concepts, also remote sensing methods were applied.

In the project, the following so-called "C_2-C_8" hydrocarbons have been measured: ethane, ethene, acetylene, propane, n-butane, i-butane, n-pentane, i-pentane, total hexane, benzene, total heptane, toluene, total octane, o,m,p-xylene, ethylbenzene and styrene. For practical reasons, model calculations have been limited to three components: benzene ("C_6"), styrene ("C_8") and ethene ("C_2"). These compounds were selected for various reasons: benzene for the concern about health effects and the combination of low and stack emission sources, while styrene is only emitted by a limited number of stack emission sources and ethene as a representative of "C_2-C_5" hydrocarbons, which are important precursors for ground-level ozone.

project activities
The project period was from 1 January 1996 till 1 February 1998. The project consists of two phases: Phase I (1/1/96-1/4/97) to develop a measuring and modelling strategy, and to select a demonstration area within the Rijnmond region, and Phase II (1/4/97-1/2/98) to demonstrate the methodology, and to report and disseminate the results of the project. The project has been completed within the budget of the project and envisaged staffing inputs.

results of phase I of the project
A modelling methodology; The developed methodology in phase I is based upon a combination of factor analysis, spatial linear regression, Bayesian statistics and the updated, short-term National Plume model. The method involves a number of steps: 1.) correction of data for background and traffic emissions, 2.) presentation of hourly measured air concentrations in accordance to wind sectors, 3.) factor analysis to identify source categories of VOC emissions, and 4.) spatial linear regression, Bayesian statistics and inverse-dispersion modelling to compute emission rates.

A measuring strategy; The developed strategy involves a triangle of three monitoring stations *outside* the industrial area to measure hourly "C_2-C_5"concentrations. This approach provides ground-level concentration differences at six wind directions in which one station serves as receptor station (down-wind of the industrial area), while the opposite station is the background station (up-wind of the industrial area). Fourteen passive sampling locations *within* and three locations *outside* the industrial area were applied to measure "C_6-C_8"concentrations. The number of locations within the industrial area was related to (expected) number of emission sources, while outside the area the locations were similar to the "C_2-C_5" monitoring stations.

A demonstration area; Within the Rijnmond region, the Botlek/Pernis industrial area was selected as demonstration with a surface of 4*2 km. Industrial activities within the Botlek/Pernis area include large-scale chemical plants, refineries and storage of oil products.

results of phase II of the project
Results; Taking into account uncertainties of meteorological and air concentrations measurements, as well as comparing three-monthly measurements in 1997 with *annual* Emission Inventory data from 1995, the analysis of benzene, styrene and ethene demonstrate that both passive and active sampling result in comparable emission rates within a factor two of the Emission Inventory data.

Data analysis of the measuring campaign indicate that the *styrene* emission rate of the most important source in Botlek/Pernis area is a factor 10 smaller compared to the EI database of 1995 (according to information from Shell, the result of recent measures to reduce styrene emissions); *benzene* emission rates of the 27 most important sources agree within a factor 2-4 with the EI database, with the exception of stack emission at 213 m height where the mixing height may influence the method and an unknown *ethene* emission source was identified. The measured two-weekly averaged emission rates of styrene and benzene show fluctuations over an order of magnitude and consequently, also ground-level air concentrations of these compounds.

conclusions
It is concluded that the results presented in this report for styrene, benzene and ethene demonstrate that the method provides adequate information on the *spatial distribution* of emission sources, *chemical profiles* of emission sources, *temporal fluctuations* of emission rates and the *reliability* of the calculated emission rates. The method can distinguish low (diffuse) and high (stack) emissions.

A second conclusion is that the most cost-effective and simple methodology to assess emission rates from low sources of "C_6 and higher VOC" (including chlorinated compounds) is based upon passive sampling *within* the industrial area. For "C_2-C_5 VOC" emissions, a triangle of up- and downwind receptor locations are required based upon hourly on-line measurements and/or active sampling.

A third conclusion is that the developed method provides an important instrument for enforcement agencies to monitor actual VOC emissions from a complex industrial sources, not only on an annual but even at a two-weekly basis. This is an important aspect in order to check the effects of measures to reduce industrial VOC emissions.

A fourth conclusion concerns VOC emission measurements by the HAWK and FTIR remote sensing techniques. It is concluded that the HAWK is not an adequate technique to estimate VOC emissions from an industrial area, due to its lack of sensitivity for "C_2-C_5 VOC", as compared to methane air concentrations. Under plant conditions with a more favourable "C_2-C_5 VOC"/methane ratio, HAWK measurements is a suitable on-line detection technique, due to its simple operation as compared to automated GC. The FTIR in combination with Bayesian statistics is a promising method to determine VOC emission rates, though (due to the relatively high detection limits) the method is more adequate for on plant measurements.

Finally, it is concluded that the objectives of the project: *to develop and demonstrate a methodology to assess VOC emissions, and to estimate the contributions by various source categories in a complex industrial area based upon ground-level VOC measurements* have been achieved. Presently, there is no need for further development of the method, but there is definitely need for more practical experiences.

dissemination
The method was discussed with (inter)national experts at two workshops organised at TNO in Apeldoorn (the Netherlands). The outcome of the project was also presented in the GENEMIS workshop at 7th October 1997 in Stuttgart in the framework of the EUROTRAC programme. Publication of the results in relevant magazines and a scientific journal are envisaged in 1998. In addition, TNO will prepare in 1998 an information sheet to be distributed to private companies, industrial associations and relevant authorities to support further application of the method.

recommendations

It is recommended to apply the method by various potential users such as:

- A local industrial authority may use the method to identify "hot spots" of VOC emissions in an industrial area *without* an Emission Inventory in order to develop a cost-effective abatement strategy in consultation with local industrial companies;
- National or regional enforcement agencies may use the method as a monitoring instrument to validate VOC emission data of the Emission Inventory from a complex industrial area in order to assess the effects of VOC emission reduction measures; and
- Private companies (chemical base, storage and refineries) may use the method (eventually in combination with the FTIR method) to assess diffuse emissions at plant scale in order to control production losses and improve maintenance schemes of for example storage tanks.

Contents

List of abbreviations

EC   European Commission

EI   Emission Inventory

FTIR   Fourier Transform Infra Red

DCMR   Environmental Protection Agency of Rijnmond

KNMI   Royal Netherlands Meteorological Institute

KWS-2000   Netherlands Programme to reduce VOC emissions

TNO   Netherlands Organisation for Applied Scientific Research

VOC   Volatile Organic Compounds

VROM   Netherlands Ministry for Housing, Physical Planning and
            Environmental Protection

1.   Introduction

1.1   Background

Air concentrations of Volatile Organic Compounds (VOC) can potentially lead to increased concentrations of ground level ozone, which may cause respiratory problems, damage to vegetation and contribute to the greenhouse effect. Next to traffic, various industrial activities are regarded as important sources for air pollution by VOC. Consequently, in the vicinity of large-scale industrial activities VOC concentrations may directly affect human health.

At European level, measures are introduced to reduce VOC emissions both from industrial and traffic sources. At national level, programmes are also initiated to reduce VOC levels in ambient air. For example, in the Netherlands the "KWS-2000" project aims at a reduction of VOC emissions in the year 2000 with 50% compared to the year 1981.

In order to evaluate the effect of emission reduction measures within industrial areas, one requires an answer to the question: Which VOC sources in an industrial area are contributing how much to ambient air concentrations in the vicinity of the industrial area? This problem is illustrated in Figure 1.1.
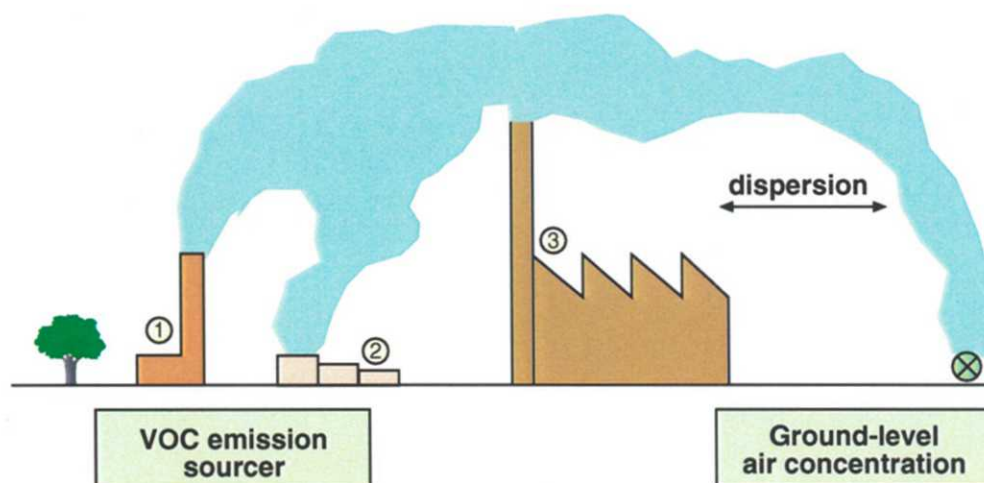
Figure 1.1   Air pollution around an industrial area.

Figure 1.1 shows VOC emissions by various sources within an industrial area from low stacks (1), diffuse emissions from storage tanks (2) and high stacks (3). After plume rise and dispersion in the atmosphere, VOC emissions result in increased VOC ground-level concentrations. In the Netherlands, the National Emission Inventory (EI) is used to collect information on VOC emissions and subsequently, in combination with dispersion models, ground-level air concentrations of VOC are computed.

The EI includes registration, location and presentation of emission data of both industrial and non-industrial sources in the Netherlands. The emission data are updated every year by TNO under a contract by National Authorities. Emissions to air and water are distinguished into *industrial source* and *collective source categories*. The central database of EI contains emissions of about 900 compounds from 700-800 major companies. For large industrial point sources the emissions are based upon detailed information of each individual plant. While emissions of small and medium-sized enterprises, as well as non-industrial sources are based upon economic data and emission factors.

However, there are constraints to compute the effect of air pollution reduction measures based upon EI data:

- *firstly*, several studies have indicated discrepancies between the "EI-based" methodology and actual ambient air measurements, which may be due to incorrect emission factors and/or un-know sources such as diffuse emissions;
- *secondly*; ambient air concentrations estimated from EI data concern *annual* average concentrations and hence, there is at least a delay of one year to provide these concentrations and no information is provided on fluctuations within a year for example during a smog-episode; and
- *thirdly;* EI data do not exist in all European countries.

For the aforementioned reasons, complementary to the "EI-based" methodology, *there is a need for an alternative method to assess VOC emissions from large-scale industrial areas*. Such an instrument may be applied i.) in European countries *without* EI data to monitor the effects of VOC emission reduction measures, and ii.) in countries *with* EI data to validate EI data, to identify unknown VOC sources and to collect more detailed and readily available information on (for example) monthly VOC emission rates.

In the framework of this project, a methodology has been developed based upon VOC ground-level air measurements to identify and quantify the contribution by various VOC emission sources from an industrial area.

1.2   Short-term objectives

The short term objectives of the project are:

1. to develop a methodology to assess VOC emissions based upon VOC ground-level measurements;
2. to demonstrate the methodology in the Rijnmond area by identification of various sources of VOC emissions and computation of the strength of their emission rates

1.3 Project Actors

TNO has been granted by the European Commission under the LIFE programme to implement the project. The project has been monitored by Mr. M. Leijendeckers of Tauw Milieu on an assignment by the European Commission.

The Netherlands Ministry of Housing, Physical Planning and the Environment (VROM), the Environmental Protection Agency of Rijnmond (DCMR) and SHELL Research Ltd., the Netherlands have supported the project by the following contributions:

- VROM contributed NLG. 250.000,-. In the framework of the VOC-emission reduction programme "KWS-2000" in the Netherlands, VROM is especially interested in an instrument to assess VOC emissions by large-scale industrial sources. The generated data may be compared with VOC emission data provided by the Netherlands Emission Inventory in order to identify "unknown" and diffuse sources.
- Under the project, DCMR has made available three of its monitoring sites to install sampling and on-line equipment, as well as air quality data collected under its routine monitoring programme. The contribution by DCMR has been estimated to be equivalent with NLG. 100.000 based upon the reduction of the originally planned inputs by TNO (i.e. staff, analysis, equipment and travelling) in phase II.
- SHELL is one of the major industries in the Rijnmond area with large-scale chemical operations, storage of oil products and refineries. SHELL Research Ltd., the Netherlands contracted SHELL, United Kingdom to perform remote sensing measurements and will make available the collected data to the project. The contribution by SHELL has been estimated to be equivalent with NLG. 100.000 based upon the reduced, planned inputs by TNO (i.e. staff, analysis, equipment and travelling) in phase II.
- TNO has managed implementation of the project and contributed by expertise, staff, equipment, chemical analytical services and models.

1.4 Set-up of the Report

In Chapter 2 the project approach and planning of activities are described. Chapter 3 provides information on the results of phase I related to development of the methodology and selection of the pilot area within Rijnmond. Chapter 4 presents the results of phase II are presented related to demonstrate the methodology in the Botlek/Pernis area. In Chapter 5, conclusions and recommendations are discussed. Chapter 6 describes dissemination activities, Chapter 7 presents authentication of the report and Chapter 8 includes references. Annex 1 gives details on the results of the measurements, while staffing and financial aspects of the project are reported in a separate document.

2. Project approach

2.1 Project methodology

In order to elaborate the project methodology, some background is provided on the general methodology to determine emission rates from ground-level measurements. This is illustrated by the single-source and multiple-sources situation, respectively

Single source situation

A Gaussian-plume model can be applied for "inverse dispersion" modelling to calculate the VOC emission rate from ground-level VOC air concentration measurements. This is relatively simple in case of a single stack and two monitoring sites up- and downwind of the emission source. The difference between VOC air concentrations measured at the two monitoring stations during an appropriate wind direction is attributed to the VOC emission source. Using the Gaussian-plume model and adequate meteorological conditions to account for the plume rise and atmospheric dispersion, the emission rate can be calculated.

Multiple-sources situation

The situation is more complex in an industrial area such as the Botlek/Pernis area, which combines various point (i.e. high and low stacks) and diffuse sources (i.e. evaporation from storage tanks, spillage and traffic). The contribution of the multitude of these VOC sources can be measured by two alternative measurement approaches by so-called *receptor* and *emission* locations. These two approaches are applied in this project and are illustrated in Figure 2.1.
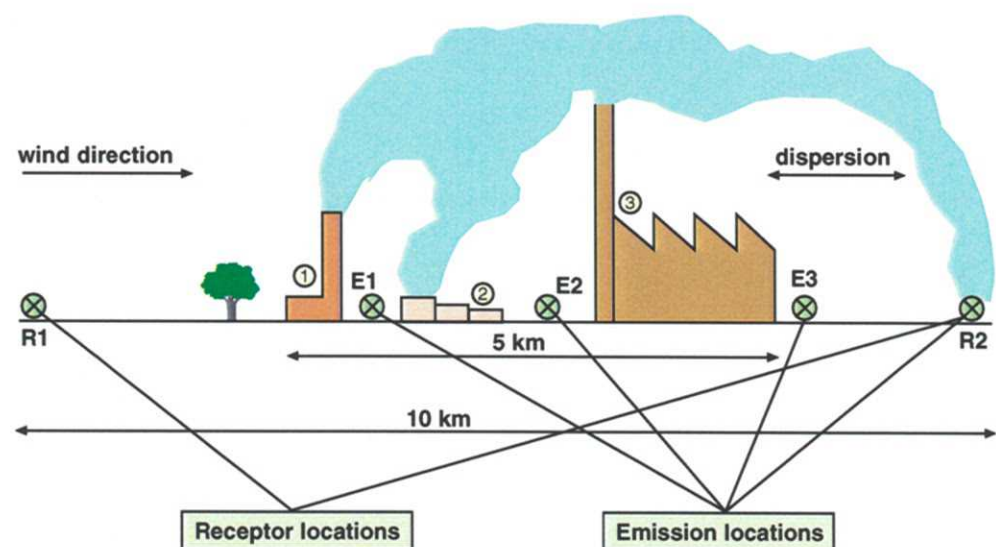
Figure 2.1   Measurement strategy in and around an industrial area.

Figure 2.1 shows VOC emissions within an industrial area by low stacks (1), dif-
fuse emissions from storage tanks (2) and high stacks (3). VOC emissions result
in increased VOC ground-level concentrations down-wind at location (R2) as
compared to the up-wind location (R1). These monitoring locations *outside* the
industrial area concern *receptor* monitoring sites. Also *within* the industrial area
ground-level VOC air concentrations are increased at for example locations E1,
E2 and E3. Monitoring stations *inside* the industrial area relate to *emission*
monitoring sites. The two measurement approaches used in this project con-
cern receptor and emission sites:

1. a triangle of three *receptor* locations around the area to maximise the col-
   lection of information on dispersion of the multitude of sources. The meas-
   urements provide hourly ground-level concentration differences at six wind
   directions in which one station serves as receptor station, while the opposite
   station is the background station. The measured concentration difference at
   appropriate wind directions now consists of the sum of contributions of sev-
   eral VOC emission sources; and

2. fourteen *emission* locations have been selected to measure two-weekly
   ground-level air concentrations with passive samplers. In this case, the air
   concentration differences between the fourteen locations and the six sam-
   pling periods, as well as the meteorological conditions provide information
   on VOC emissions.

The next step in both cases is to apply factor analysis on the measured air con-
centrations (passive sampling) or differences of measured air concentrations
(active sampling) to identify the contributing sources. The next step is "spatial
linear regression" or "Bayesian statistics" in combination with inverse disper-
sion modelling is used to calculate the emission rates of the identified emission
sources. The determined emission rates are compared to EI data to validate the
approach. Finally, the results from both the two measurement approaches are
compared, in order to recommend the most cost-effective methodology to es-
timate VOC emission sources by ground-based measurements.

remote sensing measurements

In addition to the monitoring stations at the three receptor and fourteen emis-
sions sites, also remote sensing measurements have been applied at two recep-
tor sites and at several emissions sites within the industrial area. Remote sensing
concerns direct optical air concentration measurements over an "open path"
length and provides information on plume profiles (ratio between air concen-
trations of specific hydrocarbons) of VOC emissions by typical industrial activi-
ties. Using Bayesian statistics results in quantifying emission rates of VOC emis-
sion sources. Remote sensing measurements are applied most extensively on in-
dustrial plants to determine VOC emissions for example during different pro-
duction conditions. In this project, the application of remote sensing to esti-
mate VOC emissions from a large-scale industrial area is tested.

project details

The aforementioned steps in the project methodology are further elaborated below:

- the first step is to select within the Rijnmond region, which has a size of about 40*20 km, a smaller pilot area to demonstrate the methodology. The selection is based upon considerations such as the size of the area, diversity of VOC sources and existing monitoring sites of the local environmental protection agency;
- the second step is to develop a modelling strategy in order to calculate emission rates from measured ground-level monitoring sites. This requires an one-hour, inverse dispersing model in combination with regression analysis to calculate emission rates from ground-based measurements. The outcome of this step is a modelling strategy and recommendations on the measuring strategy (frequency of sampling; number of components; number of monitoring locations; required meteorological data etc.);
- the third step is to collect a-prior information on the selected industrial area (type of industrial activities, the height and location of emission sources area and estimated VOC emission rates) in order to select the locations of *receptor and emission* sites. Subsequently, sampling and measuring equipment are installed and appropriate meteorological data collected;
- the fourth step is to demonstrate the methodology by implementing measurements followed by data analysis using the developed modelling strategy. This step results in multiplication factors for "default emission rates" of VOC emission sources from the EI and emission rates of unknown VOC sources identified in this step;
- the fifth step is to compare the results of both emission and receptor sites, and remote sensing measurements with EI data, to discuss the methodology with (external) experts and to disseminate the demonstrated methodology.

These aforementioned five basic steps in the project methodology have been used to guide project activities, which are further elaborated in the next section.

2.2 Project activities

The project duration was two years from January 1996 till February 1998. The project has been implemented following a phased approach:

Phase I was the Research and Development phase and was implemented from 1/1/1996 to 1/4/1997. Phase I was directed to develop a modelling methodology, to select a monitoring strategy and to consult national and international experts. During this phase, literature has been surveyed and models have been tested. The outcome of this phase was discussed with experts during the workshop in March 1997. This phase has been finalised by submitting the Interim Report.

In Table 2.1, the activities in phase are presented in an activity bar chart.

Table 2.1   Activity bar chart of activities implemented in phase I..

STEP	ACTIVITY	1996							1997	
		Feb	Apr	Jun	Aug	Okt	Dec		Feb	
pilot area	- consultation with local authority									
selection	- EI data collection									
	- dispersion calculations									
	- profile calculations									
	- pilot area defined									
modelling	- define specifications									
strategy	- test various models									
	- apply models on EI data of pilot area									
	- define specifications for measurements									
monitoring	- consultation DCMR									
strategy	- inspection of potential monitoring sites									
	- establish QA programme									
	- select sites, methods and frequency									
dissemination	- workshop									•
reporting	- Draft Interim Report									•
	- Final Interim report									•

The results of phase I are described in detail in Chapter 3.

Phase II was the Demonstration phase and has been executed from 1/4/1997 to 1/2/1998. Phase II was related to actual measuring activities in the Botlek/Pernis area, to process the collected data in accordance to the modelling strategy and to report the outcome of the project. This phase has been concluded with a workshop in November 1997 to disseminate the results of the project and drafting of the Final Report.

In Table 2.2, the activities in the project are presented in an activity barchart.

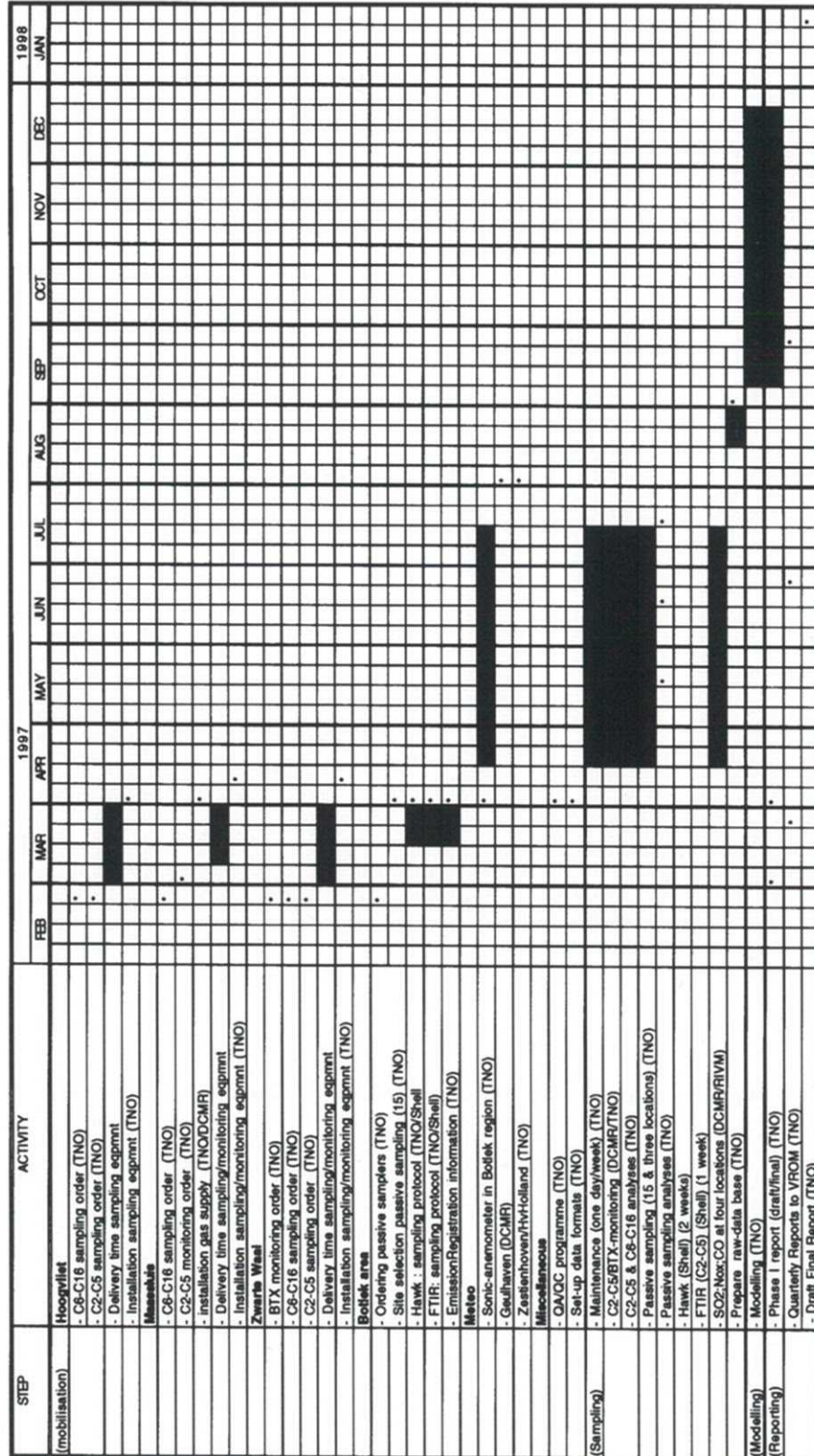Table 2.2   Activity bar chart of activities implemented in phase II.

STEP	ACTIVITY	1997 FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	1998 JAN
(mobilisation)	**Hoogvliet**												
	- C6-C16 sampling order (TNO)		██										
	- C2-C5 sampling order (TNO)	•											
	- Delivery time sampling eqpmnt												
	- Installation sampling eqpmt (TNO)												
	Maasvlie												
	- C6-C16 sampling order (TNO)	•											
	- C2-C5 monitoring order (TNO)		██										
	- installation gas supply (TNO/DCMR)			•									
	- Delivery time sampling/monitoring eqpmnt												
	- Installation sampling/monitoring eqpmnt (TNO)												
	Zwarte Waal												
	- BTX monitoring order (TNO)	•											
	- C6-C16 sampling order (TNO)	•											
	- C2-C5 sampling order (TNO)	•											
	- Delivery time sampling/monitoring eqpmnt		██										
	- Installation sampling/monitoring eqpmnt (TNO)			•									
	Botlek area												
	- Ordering passive samplers (TNO)			•									
	- Site selection passive sampling (15) (TNO)		██										
	- Hawk : sampling protocol (TNO/Shell)		•	•									
	- FTIR: sampling protocol (TNO/Shell)			•									
	- EmissionRegistration information (TNO)			•									
	Meteo												
	- Sonic-anemometer in Botlek region (TNO)			██	██	██	██						
	- Geulhaven (DCMR)						•						
	- Zestienhoven/HvHolland (TNO)			•									
	Miscellaneous												
	- QA/QC programme (TNO)						•						
	- Set-up data formats (TNO)												
(Sampling)	- Maintenance (one day/week) (TNO)		██	██	██	██	██						
	- C2-C5/BTX-monitoring (DCMR/TNO)												
	- C2-C5 & C6-C16 analyses (TNO)						•						
	- Passive sampling (15 & three locations) (TNO)					•							
	- Passive sampling analyses (TNO)												
	- Hawk (Shell) (2 weeks)						•						
	- FTIR (C2-C5) (Shell) (1 week)			██	██	██	██						
	- SO2:Nox:CO at four locations (DCMR/RIVM)												
	- Prepare raw-data base (TNO)									•			
(Modelling)	- Modelling (TNO)							•	██	██	██	██	•
(Reporting)	- Phase I report (draft/final) (TNO)	•	•	•									
	- Quarterly Reports to VROM (TNO)		•										
	- Draft Final Report (TNO)												•

The results of phase II are described in detail in Chapter 4.

3.   Results of Phase I

3.1   Selection of the project area

The project area was envisaged within the Rijnmond region. Rijnmond is located along the river Rhine in the west of the Netherlands in between Rotterdam and the North-Sea. It contains among other the harbour of Rotterdam, storage of oil products and industrial activities by refineries and chemical base plants. The size of the area is approximately 40 * 20 km, which is too large and too complex to develop a monitoring methodology. The selection of the project area was based upon location of VOC sources, variety in high and low stacks, presence of storage tanks, size of the area, strength of VOC rates, existing monitoring sites of the local enforcement authority "DCMR" and the modelling methodology. Based upon these criteria and model calculations of various potential areas, it was decided to select the centre area of Rijnmond, the so-called Botlek/Pernis area with a surface of 4*2 km. The Botlek/Pernis area, which is enclosed by DCMR's and project monitoring stations at Maassluis, Zwartewaal and Hoogvliet is presented on a map in Figure 3.1
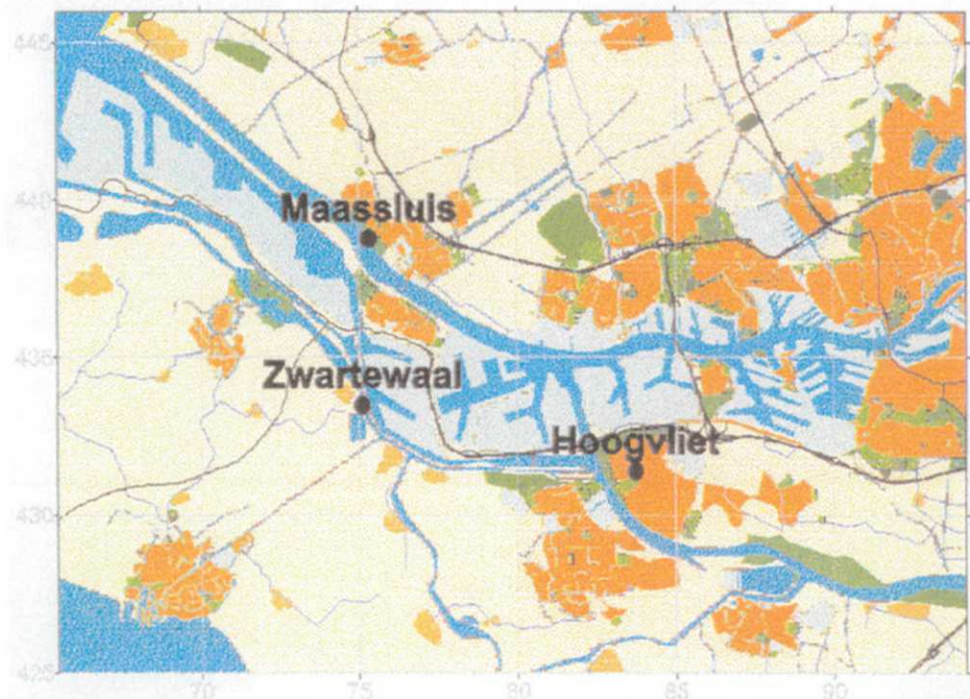

Figure 3.1   The Botlek/Pernis area and three receptor monitoring sites.

The Botlek/Pernis area is defined by the co-ordinates: 433 - 435 (South-North) and 78 - 82 (West-East).

In the following sections, information is presented on the spatial distribution of VOC emissions and most important sources in Botlek/Pernis. This information has been retrieved from the Netherlands EI and has been used to design the measurement strategy, as well as to support the interpretation of the modelling exercise. It is noted that in case of industrial areas without an EI database, the aforementioned information is collected from site-inspection and "default" emission rates of VOC compounds may be estimated from similar industrial activities elsewhere.

3.1.1   Spatial distribution of emission sources in Botlek/Pernis

EI data are used to illustrate VOC emissions in Botlek/Pernis by various source categories. In Figure 3.2, the spatial distribution of four important "individual industrial" source categories are presented.

Figure 3.2   Spatial distribution of four "individual industrial" source categories in Botlek/Pernis.

3.1.2   C$_2$-C$_8$ VOC emissions by source categories in Botlek/Pernis

The EI contains more than 900 compounds emitted by various sources in Botlek/Pernis. It is not possible to involve more than 900 compounds in this project and therefore, VOC compounds have been limited to "C$_2$-C$_8$" hydrocarbons. In section 3.3 more details are provided on the selection of the compounds.

The most important sources of the selected "C$_2$-C$_8$" VOC emissions by various source categories in Botlek/Pernis are presented in Table 3.1.

Table 3.1   Contribution of source categories to the total emission of "C₂-C₈" hydro-carbons in Botlek/Pernis

Compound	Hydro-carbon code	Emission	Contribution of source categories to VOC emissions (%)							
		(ton/y)	S1	S2	S3	S4	I1	I2	I3	others
Ethane	C₂	239	48	0	1	3	31	3	12	3
Ethene	C₂	1020	62	0	3	5	18	9	2	1
Acetylene	C₂	890	73	0	0	4	0	22	0	0
Propane	C₃	749	52	0	0	3	29	5	9	2
Propene	C₃	613	50	0	1	3	4	40	2	0
n-Butane	C₄	2003	6	0	2	0	57	4	27	4
i-Butane	C₄	672	9	0	1	0	47	10	27	4
n-Pentane	C₅	1503	10	0	2	1	51	3	29	4
i-Pentane	C₅	1228	25	0	2	1	46	2	22	2
Hexane (tot.)	C₆	2197	25	0	7	1	37	3	25	2
Benzene	C₆	629	58	0	1	6	13	10	12	0
Heptane (tot.)	C₇	998	30	0	1	2	37	2	26	2
Toluene	C₇	1697	47	0	11	3	18	10	10	0
Styrene	C₈	446	14	0	2	1	0	80	3	0
Xylene (tot.)	C8	794	73	1	6	4	0	16	0	0
Octane (tot.)	C₈	1033	52	0	1	3	23	2	17	2

In Table 3.1, the first four emission categories concern "collective sources": S1="traffic"; S2="navigation"; S3= "small companies" and S4="other emissions per inhabitant". While, the last four emission categories refer to "individual industrial sources" : I1="petrochemical industries"; I2="Chemical base industries" and I3="storage companies" and "other"= the sum of VOC emissions by other industrial sources.

From Table 3.1, it is noted that traffic (S1) is an important emission source for VOC. In the data analysis industrial emissions have been corrected for VOC emissions by traffic. In addition, it is noted that more than 80% of the industrial VOC emissions in the Botlek/Pernis area are produced by three industrial source categories: refineries (I1) , chemical base (I2) and storage tanks (I3).

Based upon the aforementioned information, it was concluded in Phase I of the project that the Botlek/Pernis area is representative for a large number of industrial areas in Europe and therefore, an appropriate area to demonstrate the methodology.

3.2   Development of the modelling strategy

3.2.1   Introduction

The objective of the modelling strategy is to calculate from ground-level air concentration measurements, the VOC emissions in the Botlek/Pernis area. This includes a number of steps: identification of VOC source categories, identification of locations and computation of emission rates of the identified sources. Various models and statistical tools are available to address these steps. In Phase I of the project, using emission rates of the EI and meteorological data from former years, various modelling strategies were applied on the Botlek/Pernis area. This resulted firstly in a modelling strategy to analyse the data collected by actual measurements and secondly provided conditions for the measurement strategy.

The basic elements in the developed modelling strategy are a combination of *dispersion* and *receptor* models:
* *Forward and inverse dispersion modelling;* In *forward-dispersion* modelling, ground-level air concentrations are calculated using emission rates and meteorological data. In *inverse-dispersion* modelling, emission rates are computed from measured air concentrations at ground-level and meteorological data. Hence, inverse-dispersion modelling is the opposite of forward-dispersion modelling and vice versa. A Gaussian-plume model describes the relation between emission rates, air concentrations and meteorological conditions. In this project, the 1997 up-dated version of the Netherlands National Plume model has been used both for hourly forward and inverse modelling. In the developed modelling strategy, forward-dispersion modelling is the first exercise to compare the *measured* with *calculated* air concentrations using EI emission data, which provides a first order estimate on the reliability of the measurements. Inverse-dispersion modelling in combination with receptor modelling is the final step in the modelling strategy to compute emission rates;
* *Receptor models* generate information on emission sources by measured air concentrations at receptor locations. In this project, factor analysis, spatial linear regression and Bayesian statistics have been used. Receptor models are mainly applied to identify sources ("factor analysis") and to estimate their contribution to air concentrations at receptor locations ("spatial linear regression" and "Bayesian statistics"). In our methodology, the latter step has been combined with inverse-dispersion modelling in order to compute emission rates of the identified VOC sources. In view of the importance of factor analysis, spatial linear regression and Bayesian statistics in the modelling approach, these methods are briefly reviewed in the next three sections.

3.2.2   Factor Analysis

The aim of factor analysis is to identify individual sources or source categories, which contribute to air concentrations at receptor locations. Prior information on potential sources (i.e. emission profiles and locations) further supports this identification.

In this project, factor analysis has been used as an instrument for an exploratory analysis of the data to identify various VOC sources. Software for factor analysis is available under standard statistical packages.

3.2.3   Spatial Linear Regression Method

Spatial linear regression results in information on the contribution of various sources to the air concentration of a single compound at various receptor locations. Hence, it provides similar results as the well-known Chemical Mass Balance (CMB) method, but main differences are that spatial linear regression uses air measurements of a single compound at various receptor locations (while CMB uses air concentrations of more compounds at one receptor location). The advantage of spatial linear regression over CMB is that there is no need for information on emission profiles.

The spatial linear regression method is based upon linear regression as applied by Mulholland and Seinfield (1995). The regression procedure requires a number of *measured* concentrations at receptor locations as well as *calculated* concentrations at the same locations by using forward-dispersion modelling, "default" EI emission rates and actual meteorological conditions. By linear regression the "default" EI emission rates are varied to give the closest resemblance between the *measured* and *calculated* concentrations. The method results in *modified* emission rates.

An important condition for the method is that the number of monitoring locations exceeds the number of emission sources. In that case the regression is over-determined and can give reliable results. For example for styrene (as will be illustrated in Chapter 4) these conditions are fulfilled, as styrene emissions are dominated by only two sources.

However, for most components in a complex industrial area such as the Botlek/Pernis area, there are a larger number of emission sources. Consequently, it is not possible to apply the relatively simple spatial linear regression method to estimate source strength of a multitude of sources and therefore, a more advanced technique is required based upon the Bayesian statistics.

3.2.4 Underdetermined problems in spatial linear regression: the Bayesian approach

As mentioned above spatial linear regression requires more known (measured concentrations) than unknown (emission rates) variables. However, in the opposite case it is still possible to extract information on emission rates from measured concentrations by using prior information present in the "default" EI emission rates. This is done by using Bayesian statistics [Buck B., Macaulay V.A. (1991): "Maximum entropy in action"].

The method calculates *modified* emission rates (starting with "default" emissions rates) from the measured concentrations. The method also calculates *uncertainties* on the modified emission rates. If the measurements strongly are determined by the emission of a certain source the uncertainty will be low. While emissions from sources with low rates and/or at large distances are only weakly represented by the measurements and therefore, the uncertainty on the most probable emission rate is large.

The aforementioned forward- and inverse-modelling and statistical tools (factor analysis, spatial linear regression and Bayesian statistics) have been tested in Phase I of the project. In Chapter 4, application of the modelling strategy is demonstrated on the measured air concentrations in and around the Botlek/Pernis area. The next activity in Phase I of the project was to develop an appropriate measurement strategy.

3.3 Development of the measuring strategy

Based upon the required inputs for the modelling strategy, the following measuring strategy was developed , which concerns the following aspects:
- *compounds;* The demonstrated methodology is valid only when the relation between emission and ground-level concentration of the compounds is linear, i.e. when the effects on the concentration of deposition and chemical conversion during transport from the source to the monitoring location are small. A second consideration in selecting hydrocarbons is the interest of policy makers and/or enforcement agencies in certain hydrocarbons, including: i.) important ozone precursors the "C_2-C_5" hydrocarbons, ii.) a toxic compound such as benzene (the "C_6" hydrocarbon), which is emitted both by traffic and evaporation from storage tanks and iii.) styrene (the "C_8" hydrocarbon) which is emitted mainly from high stacks by industrial activities. These considerations have resulted in the selection of the following "C_2-C_8" hydrocarbons: ethane, ethene, acetylene, propane, n-butane, i-butane, n-pentane, i-pentane, total hexane, benzene, total heptane, toluene, total octane, o,m,p-xylene, ethylbenzene and styrene. These compounds were measured on-line with gaschromatography or off-line analysed in TNO's

certified analytical laboratory. Shell UK implemented the remote sensing measurements.

- *monitoring period;* The monitoring period was from mid-April till mid-July 1997. A longer period was not possible due to time restrictions in the project period. A more reliable comparison with annual EI emission rates requires measurements for at least a year. However, the three months measuring campaign in this project represents a sufficient long period to demonstrate the methodology.

- *receptor sites;* ground-level air concentrations are measured at three locations at a *triangle* up- and downwind of the source area (the so-called "receptor sites") in order to determine the *total* VOC-emissions from the industrial area. The selected receptor sites are Zwarte Waal, Maassluis and Hoogvliet, which were already indicated in Figure 3.1. The distance to Botlek/Pernis is in the order of 5-10 km. The sites have been operated in cooperation with DCMR, as these sites are part of the routine monitoring network of DCMR. At the receptor sites, "C_2-C_8" *hourly* measurements have been performed by on-line monitoring and active sampling equipment. Hourly measurements are the shortest period for most of the selected hydrocarbons to be monitored in ambient air. These measurements are relatively costly, require weather-proof housing and electricity supply, and are prone to vandalism. These measurements concern the following details:
  - Three continuous so-called "BTX-monitors" have been operated at the three receptor locations. Benzene, toluene, m-xylene, o-xylene, p-xylene, ethyl benzene and styrene ("C_6-C_8") have been measured at 30-minutes sampling averages;
  - A so-called "C_2-C_5 monitor" (an automated GC) has been installed at Zwarte Waal. At the other two sites hourly samples in "Tedlar" bags have been taken for one hour at alternating hours every day between 10.00 AM and 15.00 h PM. This provides information on the diurnal variation of "C_2-C_5" air concentration differences between the three sites;
  - Each day at all the three sites hourly "C_6-C_8" samples have been collected by "Tenax" absorption tubes at the same time as the aforementioned "C_2-C_5" samples;
  - At the three sites, monthly samples have been collected by passive samplers to measure "C_6-C_8" air concentrations; and
  - Remote sensing measurements were performed by a "Hawk monitor"(Siemens) with an open path length of 500 m for two weeks in Hoogvliet and Maassluis to measure the sum of "C_2-C_5" air concentrations. It is a optical method with a light source and reflection of the light beam on a reflector. The amount of light absorbed at specific wavelength is a measure of the air concentration of a specific compound. The goal of these continuous measurements was to compare the HAWK performance with the aforementioned GC measurements to detect diurnal fluctuations of "C_2-C_5 VOC" emissions. The advantage of the HAWK monitor is that

its simple to operate under ambient air conditions compared to on-line GC measurements.

- *emission sites;* ground level concentrations were also measured within the source area in order to determine VOC-emissions with emphasis on *diffuse and low-stack* sources. The emission sites were fourteen locations within Botlek/Pernis near the most important "C_6-C_8" emission sources as identified by the Netherlands Emission Inventory. The fourteen locations are presented in Figure 3.3.
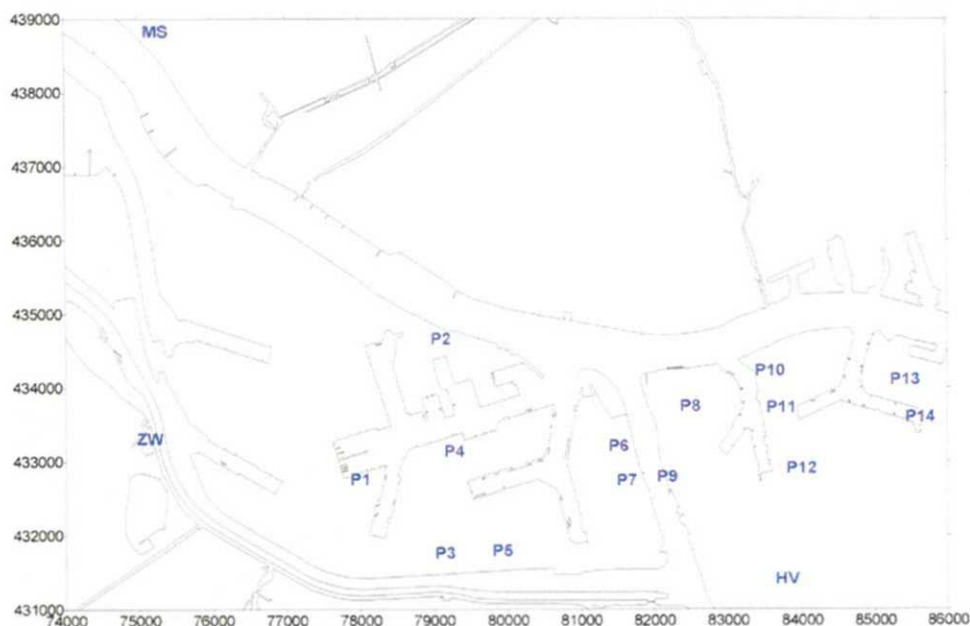
Figure 3.3   *The fourteen locations of the passive samplers within the Botlek/Pernis area.*

At the emission sites air concentrations of "C6-C8" have been collected by passive samplers by two-weekly measurements. Passive samplers are cost-effective and can be easily installed at many locations (without electricity supply) and are rarely removed during the sampling period. Two weeks are the shortest period for most components to be monitored by passive sampling in ambient air. Hence, it is difficult to link the measurements with wind directions, but it is demonstrated in this project that this disadvantage is compensated by the large spatial coverage of passive samplers. Unfortunately, no passive samplers are available for "C2-C5" components. Details of the passive samplers are as follows:

Active carbon-coated passive samplers are extracted after sampling with carbondisulfide and analysed with GC. The sampling periods of the passive samplers over a total period of three months are presented in Table 3.2.

Table 3.2   The six sampling periods of the fourteen passive samplers.

period	start	end
1	10-04-97 16:00	1-05-97 15:00
2	1-05-97 15:00	15-05-97 10:00
3	15-05-97 10:00	29-05-97 15:00
4	29-05-97 15:00	12-06-97 14:00
5	12-06-97 14:00	26-06-97 12:00
6	26-06-97 12:00	10-07-97 12:00

In total 90 air measurements were performed with the passive samplers.
In addition to the passive samplers, remote sensing was conducted during one
week to measure directly "C_2-C_5 VOC" air concentrations with a Fourier Trans-
fer Infra Red (FTIR) instrument. FTIR is based upon a infra red beam which is
reflected in ambient air on a "mirror". VOC components present in the beam
absorb infrared radiation and the relative contribution of each component (and
thus the air concentrations) can be specified. In combination with meteorologi-
cal data, a dispersion model and Bayesian statistics, a map is produced with
emitting "C_2-C_5 VOC" sources up-wind of the path length. In addition to the
location of emission sources and strength of emission rates, also the height of
the emission sources is calculated. During the one-week campaign in July 1997,
21 beam positions with a path length of 200 - 300 m were used within the
Botlek/Pernis area. The beam positions are indicated in Figure 3.4.

1 km
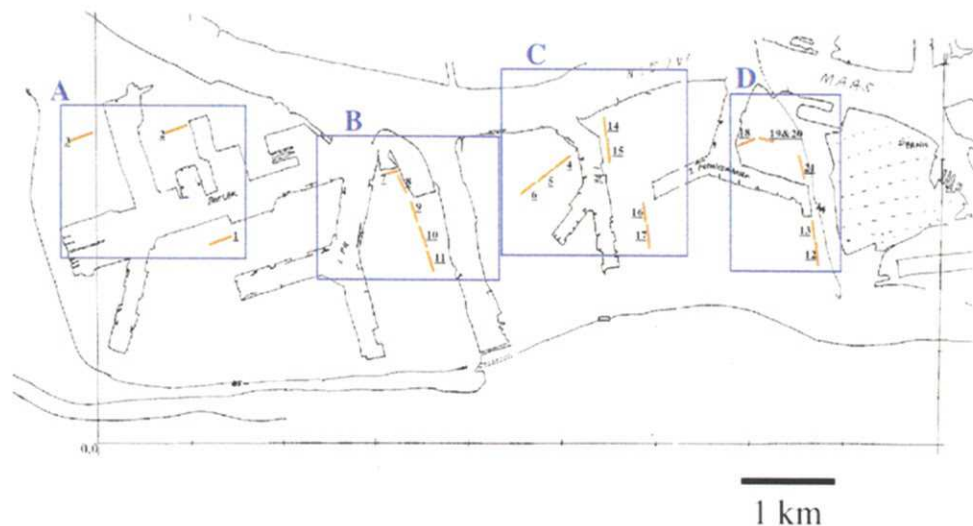
Figure 3.4   The beam positions of the FTIR measurements in the Botlek/Pernis area.

- *meteorological data;* Meteorological data have been retrieved from the National Meteorological Network at two locations: Airport Rotterdam (about 10 km north-east from the Botlek/Pernis area) and Geulhaven at the centre of Botlek/Pernis. The latter only provides windspeed and -direction, while at the former a "complete" set of meteorological parameters are collected, as required for the short-term National Plume model.

In the next chapter the results of the measurements and modelling are presented in order to demonstrate the methodology.

4.   Results of Phase II

4.1   Introduction

The results of the VOC air concentration measurements at the three receptor sites: Hoogvliet, Maassluis and Zwartewaal, and the fourteen emission sites are enclosed in Annex I. Due to reporting restrictions, *the presentation of the modelling results is limited to styrene, benzene and "C_2-C_5" hydrocarbons with emphasis on ethene.* These components best represent the methodology for the following reasons:

- *styrene,* as the number of emission sources is limited and therefore this compounds illustrates a relatively simple situation to compute emission rates;
- *benzene* has been selected because of its health effects and the large number of low and high emission sources; and
- "C_2-C_5" emissions are related to the ozone-forming potential of these compounds. "C_2-C_5" hydrocarbons include ethane, ethene, acetylene, i,n-butane and i,n-pentane. For presentation reasons, the case for "C_2-C_5" is focused on ethene.

In the following five sections of this chapter, *firstly* the meteorological conditions during the measuring period are presented (section 4.2), the *second section* concerns correction of the measured air concentrations for large-scale transport of "background" polution and traffic emissions (section 4.3), and followed by *three sections* on *styrene (section 4.4), benzene (section 4.5)* and C_2-C_5, *with emphasis on ethene* (section 4.6). The presentation in the latter three sections 4.4-4.6 follows a schematic approach:

- firstly, ground-level air concentrations at the receptor and emissions sites are estimated by forward-dispersion modelling using actual meteorological conditions and emission rates of the Emission Inventory of 1995. The results are compared with actual measurements of ground-level air concentrations of styrene, benzene and ethene. The outcome provides a "first order" estimation of the reliability of the measurements;
- secondly, based upon the ground-level measurements of both the receptor and emission sites, the meteorological conditions during the measurements and the modelling strategy, styrene, benzene and ethene emission sources are identified and subsequently the emission rates for each compound is calculated. This is the actual demonstration of the methodology.; and
- thirdly, each section is finalised with conclusions.

4.2   Meteorological conditions

Average meteorological data from half April till half July 1997 at Airport Rotterdam concern: temperature 14 °C, wind speed 4 m/s, wind direction south/south-east and rain intensity 0.1 mm/h. These data reflect "normal" meteorological conditions for this season in the Netherlands.

Wind directions during the sampling period is a critical meteorological parameter for transport of air pollutants from emission sources to monitoring sites. In Figure 4.1 frequency distributions are presented of wind directions at each of the six two-weekly sampling periods of passive samplers in the Botlek/Pernis area.
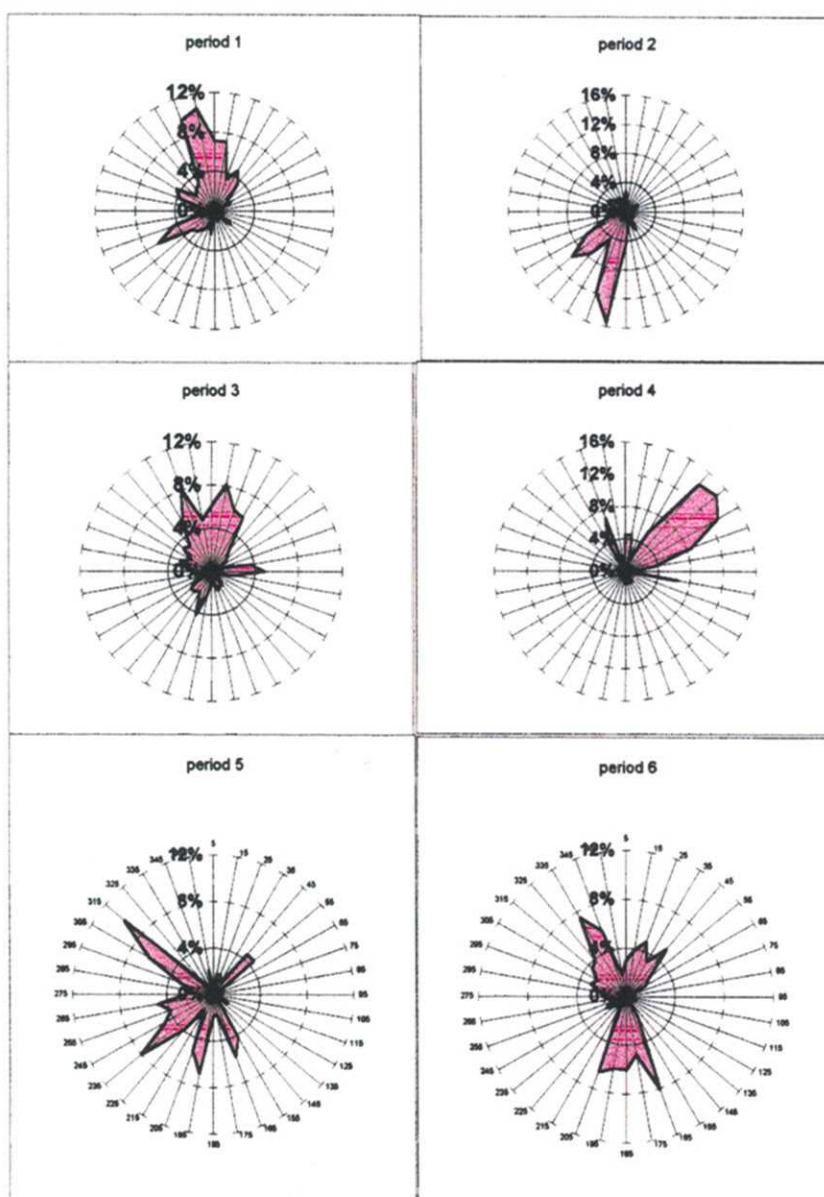

Figure 4.1   Frequency distribution of wind directions at Botlek/Pernis in the period half April to half July 1997 distinguished in six two-weekly periods.

Figure 4.1 shows that during the six two-weekly sampling periods for the five periods: 1-4 and 6, more than 50% of the time the wind direction is concentrated in a window of about 20 degrees. Consequently, air concentrations measured by passive sampling (with a sampling period of two weeks) are better correlated with VOC emissions in the up-wind direction than a-prior expected.

4.3 Correction for background and traffic emissions for passive and active sampling

4.3.1 Passive sampling results: styrene and benzene

In order to assess the contribution of *industrial* VOC emissions from the Botlek/Pernis to air concentrations measured by passive samplers at the 14 sites within the Botlek/Pernis area, the measured concentrations need to be corrected for contributions by the "background" and traffic emissions.
Background concentrations; The large-scale "background" has been determined by hourly measurements using "Tenax" sampling tubes at the three receptor sites. Each site probes a wind sector with wind directions directed away from the Botlek/Pernis area. Averages for these sectors have been calculated for styrene and benzene. Using the distribution of the windsectors for all six periods of the passive samplers (see Figure 4.1) , background concentrations have been calculated by weighted avarages. Table 4.1 shows the results for benzene and styrene.

Table 4.1   *Background air concentrations of benzene and styrene in $\mu g/m^3$ at the receptor sites Maassluis, Hoogvliet and Zwartewaal at three background windsectors (315-90, 90-215 and 215-315) for the six periods of passive sampling.*

| | Maassluis | Hoogvliet | Zwartewaal | benzene | styrene |
	315 - 90	90 - 215	215 - 315	($\mu g/m^3$)	($\mu g/m^3$)
period 1	59%	13%	28%	1.3	0.4
period 2	19%	45%	36%	1.6	0.3
period 3	61%	23%	16%	1.4	0.4
period 4	81%	16%	3%	1.4	0.4
period 5	31%	30%	39%	1.4	0.3
period 6	46%	39%	16%	1.6	0.4

The results show that variation of the *background* concentrations of benzene and styrene at various wind directions for the six periods is small.

Traffic contribution; The measured air concentrations have also been corrected for the contribution of traffic emissions. The profile of traffic emissions has been determined by TNO in Berlin and Rotterdam in earlier studies in 1996/97. The profile of traffic emissions includes all components measured by the passive samplers in Botlek/Pernis. Comparison of the traffic profiles and the profiles of the air concentrations measured by the passive samplers indicates that the contribution of 123-trimethylbenzene by industrial sources in the Botlek/Pernis area is negligible. *Therefore, it is assumed that the air concentration of 123-trimethylbenzene in the Botlek/Pernis area is determined for 100% by traffic emissions.* Using the traffic profile and specifically the ratio benzene/123-trimethylbenzene and the ratio styrene/123-trimethylbenzene, the traffic contributions to benzene and styrene have been calculated for each of the six periods and for each of the fourteen pasive samplers. The results for benzene are shown in Table 4.2.

Table 4.2   *Traffic contribution to benzene air concentrations at the 14 locations (P1-14) in the Botlek/Pernis area during six periods(period 1-6) in $\mu g/m^3$.*

	period 1	period 2	period 3	period 4	period 5	period 6
P1	0.00	0.00	0.00	0.01	0.00	0.00
P2	0.00	1.79	0.00	1.63	0.00	0.00
P3	0.00	0.00	0.00	0.19	0.00	0.00
P4	0.38	1.13	0.39	1.33	0.13	0.13
P5	0.56	0.00	0.26	0.86	0.00	0.00
P6	2.23	1.84	2.94	2.28	1.82	1.13
P7	1.41	0.78	1.15	1.19	0.74	0.15
P8	0.64	0.00	0.88	1.98	0.64	0.24
P9	0.52	0.00	0.75	1.19	0.00	0.00
P10	0.44	0.70	1.00	2.11	0.24	0.24
P11	1.66	0.93	2.17	3.56	1.29	1.24
P12	0.99	0.34	1.66	2.93	0.45	0.70
P13	0.97	1.59	1.41	2.67	0.99	0.73
P14	0.44	0.85	0.97	0.79	0.46	0.00

Using the data in Table 4.2, it is calculated that the relative contribution of traffic to benzene concentrations within the Botlek/Pernis area is less than 20% for all concentrations exceeding 5 $\mu g/m^3$ benzene.

Analogous to the benzene concentrations, also for styrene the traffic contribution has been calculated. For styrene, the results indicated that within the Botlek/Pernis area the traffic contribution to styrene is less than 10 % for all concentrations exceeding 2 $\mu g/m^3$ styrene. From these results, it is concluded that the air concentrations of benzene and styrene in the Botlek/Pernis area are determined for more than 80 % by local industrial emissions.

In the analysis in the sections 4.4 and 4.5, the "background- and traffic-corrected" air concentrations of passive sampling results are used and hence, only the contributions by the Botlek/Pernis area to the air concentrations at the fourteen sampling locations are taken into account.

4.3.2 Direct monitoring (styrene and benzene) and active sampling (ethene) results

The approach to correct for background concentrations and traffic in case of hourly measurements at Zwartewaal, Hoogvliet and Maassluis differs from the described approach on passive sampling. The air concentration measurements at these monitoring locations can be correlated with the wind direction during sampling and hence, relevant wind sectors can be assigned with the Botlek/Pernis area in between the up- and down-wind locations. Subsequently, the background and traffic contributions to styrene, benzene and ethene air concentrations have been reduced by using the *differences of the measured air concentrations*. The relevant wind sectors for the three locations are as follows (see also Figure 3.1):

- *Hoogvliet*; the relevant wind sector is 270 - 90 with Hoogvliet down-wind of Botlek/Pernis, while the measurements at Maassluis serve as the up-wind location;
- *Maassluis*; the relevant wind sector is 90 - 180 with Maassluis down-wind of Botlek/Pernis, while the measurements at Hoogvliet serve as the up-wind location; and
- *Zwartewaal*; the relevant wind sector is 45-90 with Zwartewaal down-wind of Botlek/Pernis, while the measurements at Maassluis serve as the up-wind location;

In the analysis in the sections 4.4-4.6 of the active sampling results, *the air concentrations differences in the relevant wind sectors at the three locations Hoogvliet, Zwartewaal and Hoogvliet have been applied*. Hence, only the contributions by the Botlek/Pernis area to the air concentrations at the three locations are taken into account.

4.4 Styrene

In this section, styrene is used to demonstrate the methodology.

4.4.1 Quality check of *passive_*sampling data by comparing with EI data

The EI data for styrene shows a limited number of individual sources (22) in the Botlek/Pernis area, as illustrated in Figure 4.2.
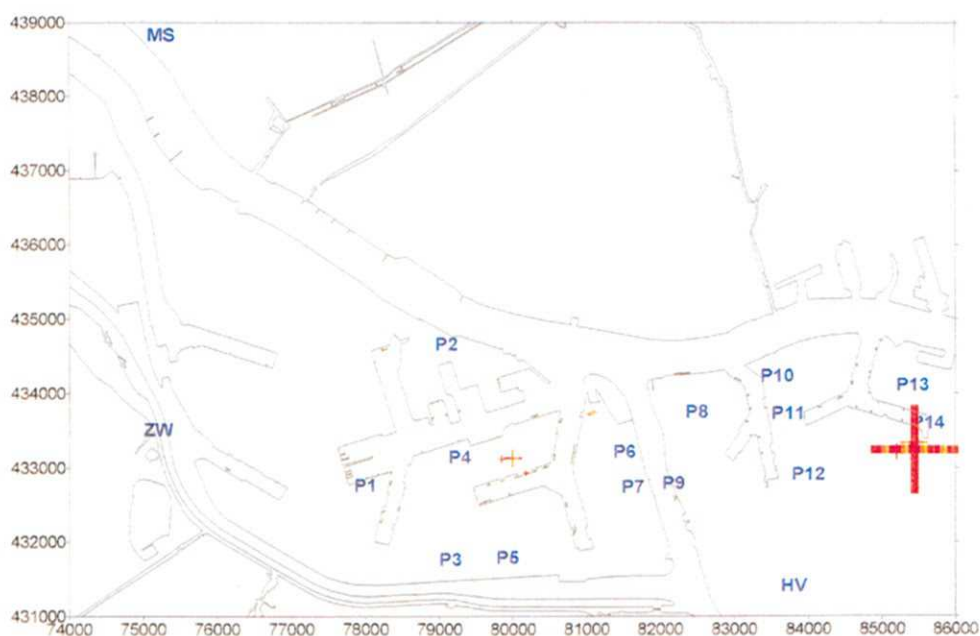
Figure 4.2 *Fourteen passive sampling locations and emission sources of styrene according to the Emission Inventory 1995. The scale of the crosses is proportional to the square root of the annual emission rate. The strongest separate source has an annual total emission of 250 ton of styrene per year.*

The most important sources are concentrated in two areas, the so-called "sources 1 and 2". *Source 1* consists of ten separate sources emitting a total of 360 ton of styrene per year and *source 2* includes three sources close together emitting a total of 14 ton of styrene per year. Receptor locations of the passive samplers P13 and P14 are located near source 1 , while receptor location P4 is located near source 2. Other styrene sources in the Botlek/Pernis area only contribute limited amounts to the styrene concentrations at the receptor sites and are therefore not included in the analysis.

Using the EI emission rates for source 1 and source 2, the actual meteorological conditions and the National Plume model, air concentrations of styrene at the fourteen receptor locations for the six periods have been calculated. These values are compared to the measured styrene concentrations (corrected for the background and traffic contributions, as described in section 4.3.1). The deviations are in general within a factor two, which is regarded a fair correlation.

4.4.2   Quality check of *active* sampling data by comparing with EI data

The styrene air concentrations have also been measured on a hourly basis at Maassluis and Hoogvliet. Therefore, it is possible to link air concentrations with wind directions during the sampling periods. From a first exercise in the analysis it was learned that the results improved when only air concentrations

were used which were measured at wind speeds larger than 3 m/s. Analogous to the section above, EI data on the emission of styrene within the Botlek/Pernis area have been used to calculate the air concentrations of styrene at Maassluis and Hoogvliet. Figure 4.3a and 4.3b shows the measured and calculated concentrations of styrene for Hoogvliet and Maassluis, as a function of wind direction.
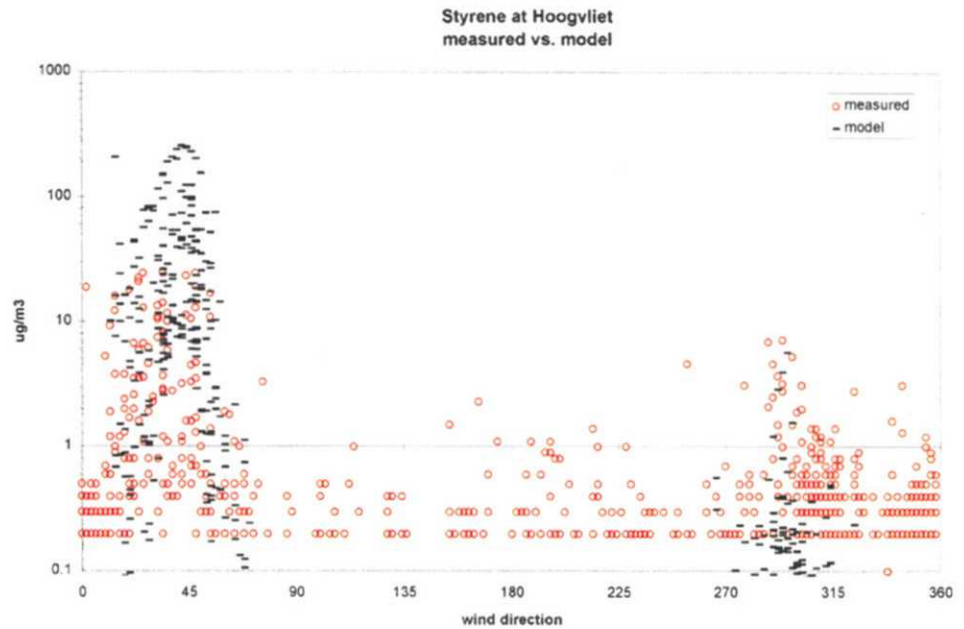

Figure 4.3a   The measured and calculated concentrations of styrene at Hoogvliet as a function of the wind direction.
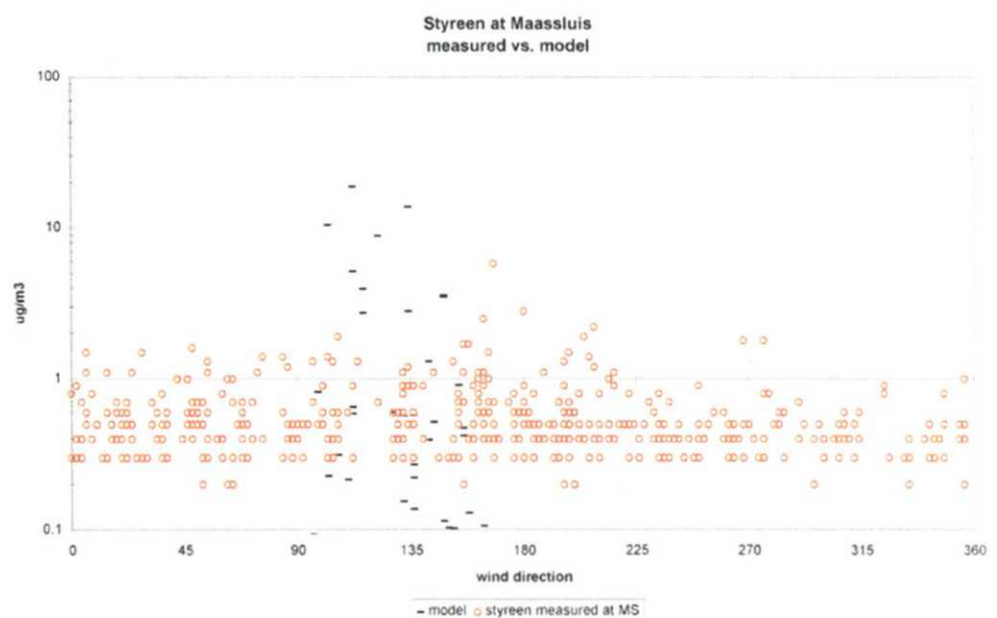
Figure 4.3b   The measured and calculated concentrations of styrene at Maassluis as a function of the wind direction.

Figures 4.3a and 4.3b illustrate that in Hoogvliet and Maassluis the styrene air concentrations are increased in the down-wind sectors of the Botlek/Pernis area respectively in the sectors 270-90 and 90-180. It is also noted that in both locations only about 25% of the air concentrations of styrene are above the detection limit of 1 µg/m^3. In Hoogvliet (Figure 4.3a), both the measured and model calculations indicate two styrene emission sources: one at north/north-east (windsector: 0-45) and the other at north/north-west (windsector: 270-315). In Maassluis (Figure 4.3b) both the measured and model calculations (though with less agreement than in Hoogvliet) indicate a styrene source south/south-east (windsector: 120-180).

In view of the locations of the two styrene emission sources and their emission rate, as shown in Figure 4.2, and the orientation and distances of Hoogvliet and Maassluis to both these styrene sources, it is concluded that the EI data in combination with model calculations agree with the hourly active measurements.

4.4.3 Estimate of styrene emission rates using spatial linear regression and *passive* measurements

The methodology developed in this project to determine styrene emission rates of the two sources 1 and 2 from air measurements with *passive* samplers is demonstrated as follows. Spatial linear regression has been applied for each of the six sampling periods using background and traffic corrected values. This results in multiplication factors to modify the EI default emission strengths of the aforementioned source 1 and source 2. The regression is adequate as the number of receptor locations is larger than the number of sources, respectively, 14 and 2. Figure 4.4 shows the result for period 2 with a correlation coefficient of 0.98.
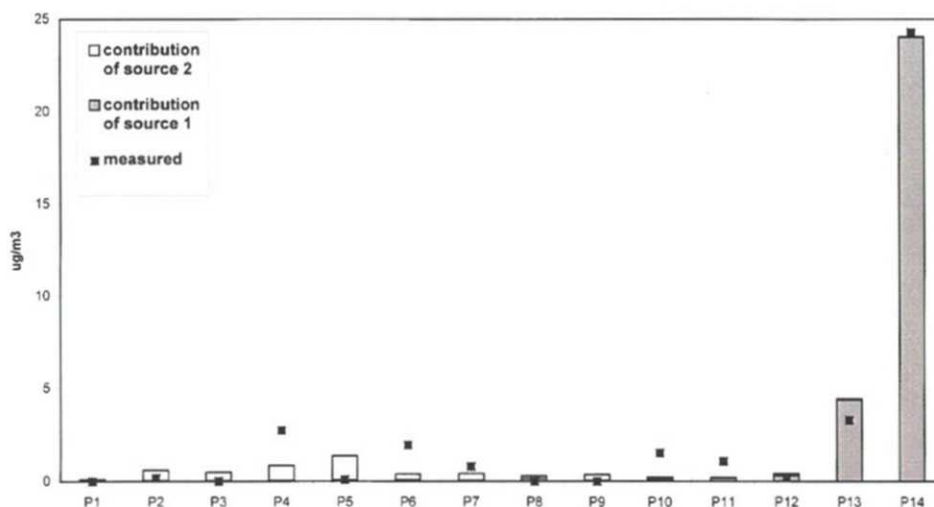

Figure 4.4   Measured and calculated concentrations of styrene for period 2 at fourteen receptor locations.

Figure 4.4 shows that the agreement of the passive sampling results at locations P1 to P14 with the calculated results is quiet good. The optimal fit with a correlation coefficient of 0.98 in Figure 4.4 was achieved with multiplication factors of 0.19 and 2.72 of the EI "default" emission rates for, respectively, source 1 and 2.

In Table 4.3, the results of the calculated multiplication factors for the EI emission rates of both the styrene sources 1 and 2 during the six periods are shown. Also, the correlation coefficients for the six fits are presented to illustrate the "goodness of fit" for each of the six periods.

Table 4.3   Results of spatial regression calculation of styrene using two sources 1 and 2 and the measured air concentrations at fourteen receptor locations. The multiplication factors for the EI emission rates are shown, and the quality of the fit (the correlation coefficient).

	Source 1	error source 1	source 2	error source 2	correlation coefficient
period 1	0.47	0.11	0.25	0.74	0.46
period 2	0.19	0.01	2.72	1.52	0.98
period 3	0.06	0.01	0.74	0.71	0.59
period 4	0.24	0.05	2.86	1.02	0.61
period 5	0.42	0.03	1.42	1.66	0.93
period 6	0.05	0.01	0.88	0.71	0.71

From the results presented in Table 4.3 it is concluded that:
- Source 1 appears to be *overestimated* by the EI emission rates by a factor of 2 (period 1 and 5) to 20 (period 6). The emission of source 2 is comparable to the EI emission rates within a factor four *overestimation* (period 1) to a factor 3 *underestimation* (period 4). The results indicate that styrene emissions and consequently air concentrations at ground-level fluctuate over the period of six two-weekly measurements from a factor 2 - 20 for source 1 and 0.3 - 3 for source 2 as compared to the EI emission rates;
- The relative error in the calculation of the multiplication factors of source 2 is larger than for source 1. This is largely due to the lesser quality of the fit for receptor locations close to source 2. The quality of the fits, indicated by the correlation coefficient in Table 4.3, is excellent for period 2 and 5 but worse for the other periods. It is concluded that receptor locations (to) close to the emission sources do not result in adequate fits.

4.4.4   Estimate of styrene emission rates using spatial regression and *active* measurements

Analogous to the section above, also with the hourly active measurements collected at Maassluis and Hoogvliet a spatial linear regression has been performed. The spatial regression results in multiplication factors of the emission rates of

sources 1 and 2 in the Botlek/Pernis area. The spatial regression results are presented in Table 4.4

Table4.4   *Results of the spatial regression calculation of styrene using two sources 1 and 2 and the measured air concentration differences during relevant windsectors at Hoogvliet and Maassluis. The calculated multiplication factors for the EI emission rates are shown , and the quality of the fit (the correlation coefficient).*

	Multiplication factor	correlation coefficient
Source 1	0.1 - 0.2	0.41
Source 2	4- 6	0.85

Analogous to the passive sampling results, also the active sampling results indicate that the emission rate of source 1 is *overestimated* by the EI with a factor 5 - 10, while source 2 seems to be *underestimated* by the EI with a factor 4 - 6.

4.4.5   Discussion and conclusions

The results of styrene demonstrate that with prior information on emission rates and locations (the so-called "default" EI values), a sufficient number of passive sampling locations and application of spatial linear regression, the method provides information on *temporal fluctuations* of emission rates (in accordance to the sampling period) and the *reliability* of calculated emission rates. This type of information is not available from EI emission data based upon *annual* emission rates.

Comparing the results of the hourly measurements in Table 4.4 with the results of passive sampling in Table 4.3 demonstrates that both the methods give comparable values for the multiplication factors of the EI emission rates. Considering the facts that the two methods use different measuring techniques (passive versus active sampling), different receptor locations (fourteen locations within the Botlek/Pernis area versus two locations outside the Botlek/Pernis area) and different dispersion calculations (two-weekly averaged versus hourly meteorological conditions) this agreement in the results provides confidence in the developed methodology.

4.5   Benzene

This section demonstrates the methodology in the case of benzene emissions from the Botlek/Pernis area.

4.5.1 Quality check of *passive* sampling data by comparison with EI data

The EI lists 184 individual sources of benzene in the Rijnmond area. The most important sources are shown in Figure 4.5. The size of the symbols is linear to the square root of the annual emission rate of benzene.
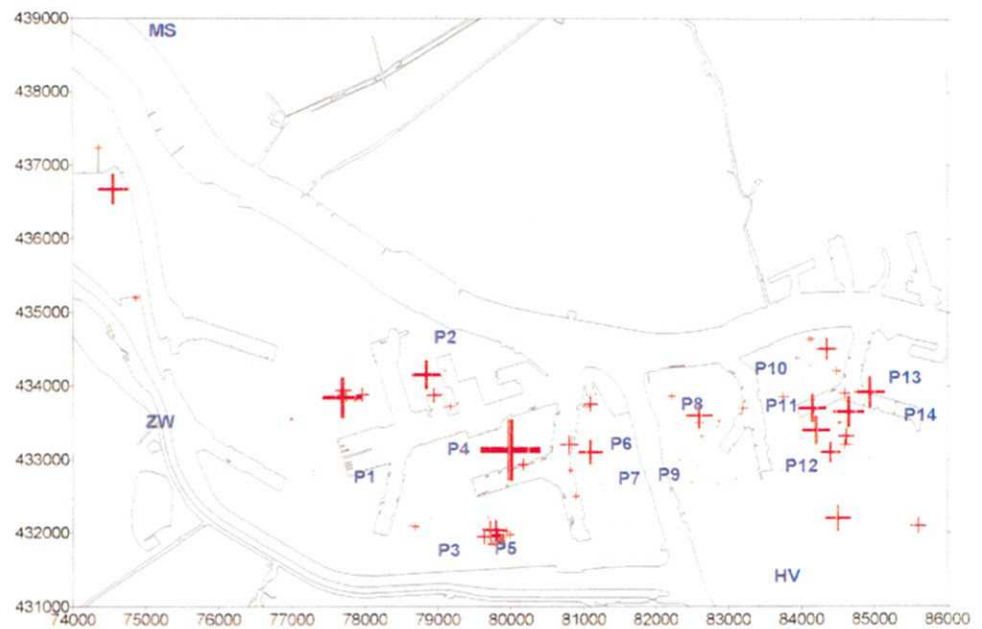
Figure 4.5   *Benzene emission sources in the Rijnmond area according to the EI.*

The strongest source (at x-coordinate: 800 and y-coordinate: 433) has an emission rate of almost 40 ton benzene per year. Major industrial benzene sources include refineries, chemical industry and storage tanks. From the EI it is known that the 22 strongest emission sources all emit benzene at a low height (storage tanks), while the two elevated sources rank 20 and 26 with heights of respectively, 213 and 40 m.

Figure 4.6 shows the strongest 27 sources of benzene in the Botlek/Pernis area by their ranking number: number 1 is the strongest source, while number 27 is the weakest.
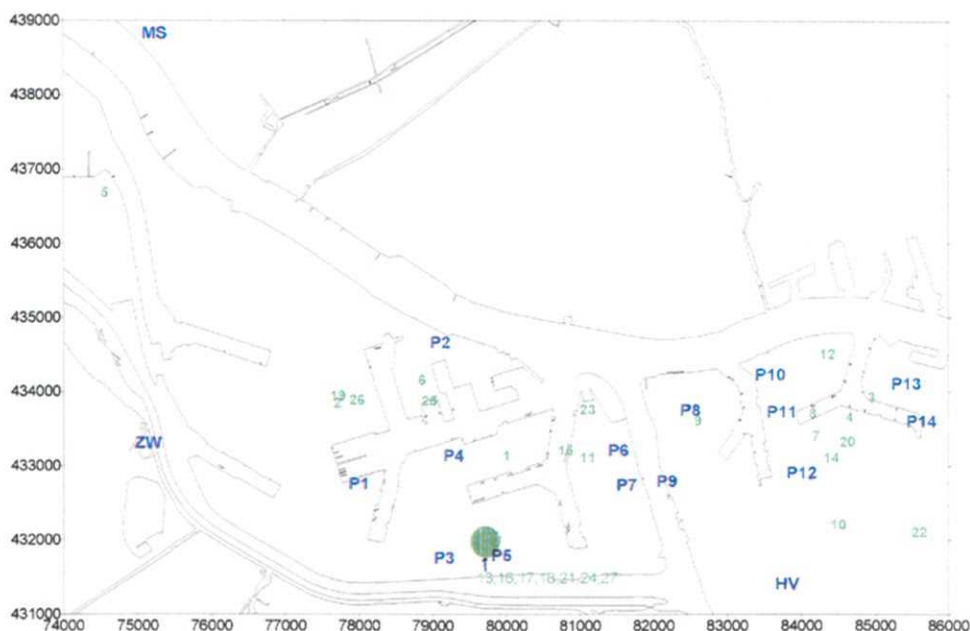
Figure 4.6   Benzene emission sources in the Botlek/Pernis area according to their EI
emission rate (1-27) and the location of the fourteen receptor locations
(P1-P14).

For each of the six sampling periods, the benzene air concentrations have been
calculated at each of the fourteen receptor points using the 27 benzene emis-
sion sources, actual meteorological conditions and the National Plume model.
As an example, Figure 4.7 shows for period 2 at each receptor location the cal-
culated and measured air concentration of benzene. The measured concentra-
tions have been corrected for background and traffic contribution, as described
in section 4.3.1
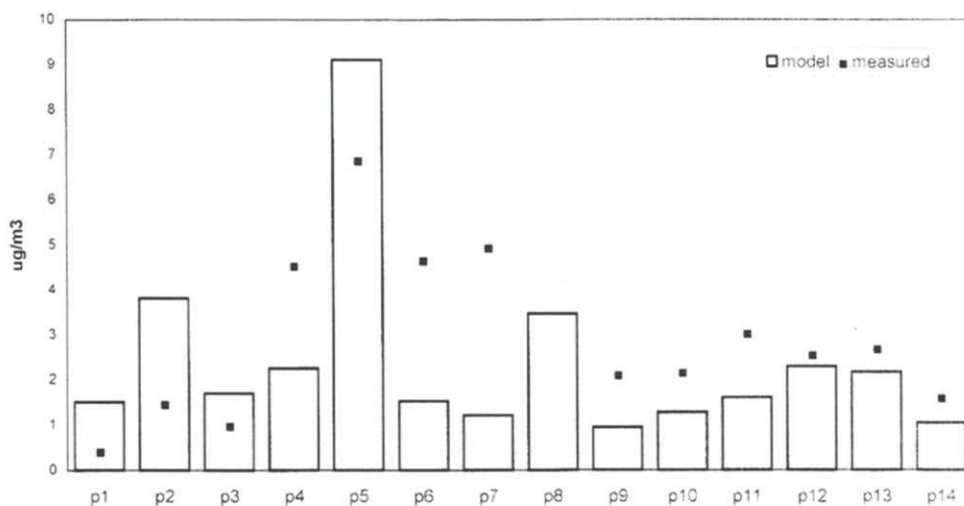
Figure 4.7   Benzene air concentrations calculated and measured values at the fourteen
receptor locations in the Botlek/Pernis area in period 2.

(Note that in Figure 4.7, the air concentration of benzene in period 2 at loca-
tion 8 is missing, due to loss of the passive sampler). Figure 4.7 illustrates that
measured and calculated concentrations for period 2 agree reasonably well, with
a few exceptions. Similar to period 2 also the results of other periods have been
compared with EI data. From this comparison, it is concluded that passive sam-
pling results agree reasonable with EI calculated values during the three-
monthly measuring campaign.

4.5.2 Quality check of *active* sampling data by comparing with EI data

Analogous to the styrene analysis, also benzene concentrations measured by ac-
tive measurements at Hoogvliet, Maassluis and Zwartewaal have been analysed.
In line with the discussion in the section on passive sampling, only the 27
strongest sources in the Botlek/Pernis area have been used to calculate the air
concentrations at all hours of the measuring period in Hoogvliet, Maassluis and
Zwartewaal.

At Hoogvliet, Maassluis and Zwartewaal, the air concentrations of benzene in
the wind sectors representing transport of air pollution from the Botlek/Pernis
area to the three monitoring locations are elevated both for measured and EI-
calculated values. It is concluded that despite differences in the level of air con-
centrations of benzene, both the hourly measured and the EI calculated air con-
centrations agree in identification of benzene sources.

4.5.3 Estimate of benzene emission rates using Bayesian statistics and *passive* measurements

Analogous to the styrene exercise, the method is demonstrated to calculate
emission rates of benzene sources from air concentration measurements at the
fourteen receptor locations. Again, the EI emission rates are treated as
"default" values and multiplication factors for the emission rates are calculated
to fit the measurements. The number of unknowns (27), which equals the num-
ber of multiplication factors for the 27 emission sources, *exceeds* the number of
known parameters (14), which equals the number of measured benzene concen-
trations at fourteen receptor locations. Therefore, a spatial linear regression as
performed for styrene in section 4.4.3 is not possible, and consequently, the
Bayesian method referred to in section 3.2.4 has been applied. Figure 4.8 shows
multiplication factors for the 27 source emission rates of benzene including the
uncertainty as error bars for period 2.
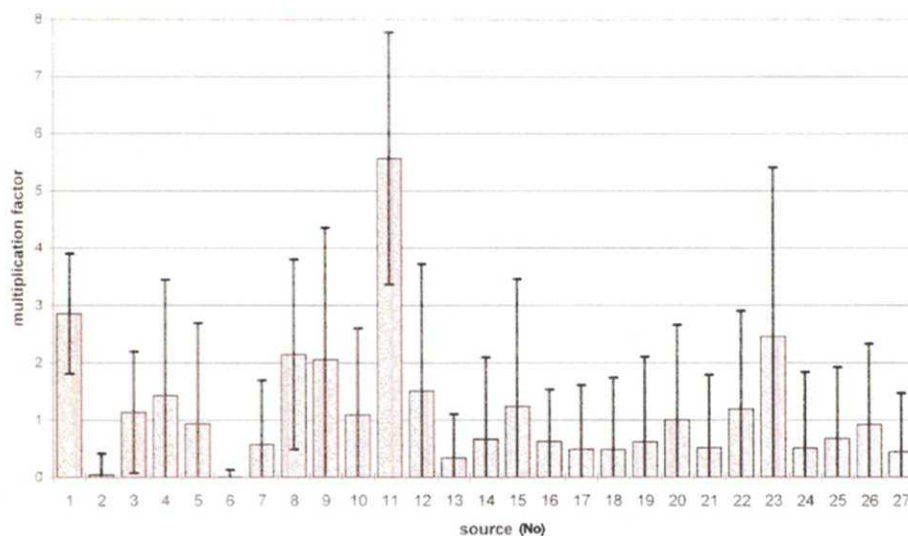
Figure 4.8   *The 27 multiplication factors for the EI emission rates of the 27 emission*
sources of benzene in period 2 calculated with Bayesian statistics.

Figure 4.8 illustrates that in period 2 the measurements only restrict four
sources (1,2, 6 and 11) to values deviating significantly from unity. Of the
other sources the measurements in this period contains little information, al-
though the results suggests a lower emission rate than the EI default values.
Similar to period 2 also for the other two-weekly periods, the multiplication
factors of the EI default values have been calculated.

The results of the average emission rates in ton benzene per year for the 27
sources in the Botlek/Pernis area and the range of measured benzene air con-
centrations during the six periods at the fourteen passive locations, are pre-
sented in Figure 4.9.

Figure 4.9   *Benzene emission rates in ton/year of the emission sources in the Bot-
              lek/Pernis area calculated from the results of passive sampling, as indicated
              by the range of benzene air concentrations ($\mu g/m^3$).*

In Table 4.5, the "default" EI emission rates and the multiplication factors of
these rates as computed from the passive sampling results are presented. Also,
information on the emission height, as retrieved from the EI database is pro-
vided.

Table 4.5   The height of emission sources, the EI emission rates of benzene in ton/year
and multiplication factors of the EI emission rates computed from passive
sampling results.

source	EI Annual emission (ton/year)	passive factor		height (m)
1	39	0	± 0	< 10
2	18	0	± 0	< 10
3	10	0.1	± 0.1	< 10
4	10	0.1	± 0.2	< 10
5	10	–	–	< 10
6	9	0	± 0	< 10
7	9	0	± 0	< 10
8	8	0.6	± 0.4	< 10
9	8	0	± 0	< 10
10	7	0.5	± 0.4	< 10
11	7	1.6	± 0.4	< 10
12	5	1.9	± 0.7	< 10
13	4	0.4	± 0.4	< 10
14	4	0.3	± 0.4	< 10
15	4	0	± 0	< 10
16	4	0.9	± 0.4	< 10
17	3	0.8	± 0.6	< 10
18	3	0	± 0	< 10
19	3	0.4	± 0.5	< 10
20	3	–	–	213
21	3	0	± 0	< 10
22	3	–	–	< 10
23	2	2	± 0.9	< 10
24	2	–	–	< 10
25	2	–	–	< 10
26	2	–	–	40
27	2	0	± 0.1	< 10

It is noted in Table 4.5, that for a number of sources the multiplication factor
for the emission rate is calculated as zero values (sources:1, 2, 6, 7, 9, 15, 18
and 21). This result of the statistical analysis indicates that these sources are
not contributing to the air concentrations of benzene at the fourteen receptor
locations. For sources 5, 20, 22, 24-26, no multiplication factor is provided as
the uncertainty in the values is too large. Hence, the sources are too far from
sampling locations or too high to contribute to ground-level concentrations.
Sources 16 and 17 show factors within an order of magnitude from unity, which
indicates that the emission rates are *equal* to default EI values. Sources 11, 12
and 23 are *underestimated* by the EI, while the other sources 3, 4, 8, 10, 13,
14, 19 and 27 all show values less than unity, which is an indication of *overes-
timation* by the EI of actual benzene emissions.

It is concluded that the measured air concentrations of benzene by passive sam-
plers *within* the industrial area provides a monitoring instrument to control
benzene emissions at *two-weekly frequency* , especially by sources emitting at
low heights: storage tanks and other diffuse emissions.

4.5.4   Estimate of benzene emission rates using Bayesian statistics and *active* measurements

Again analogous to the styrene exercise, the method is demonstrated to calcu-
late emission rates of benzene sources from hourly air concentration measure-
ments at Maassluis, Hoogvliet and Zwartewaal. The EI emission rates are
treated as default values and "multiplication factors" for the emission rates are
calculated to fit the measurements. Similar to the passive sampling results, spa-
tial linear regression as performed for styrene in section 4.4.3 is not possible,
and consequently, the Bayesian has been applied.

The results of the average emission rates in ton benzene per year for the 27
sources in the Botlek/Pernis area and the windroses at Maassluis, Hoogvliet and
Zwartewaal of the average, hourly measured benzene air concentrations during
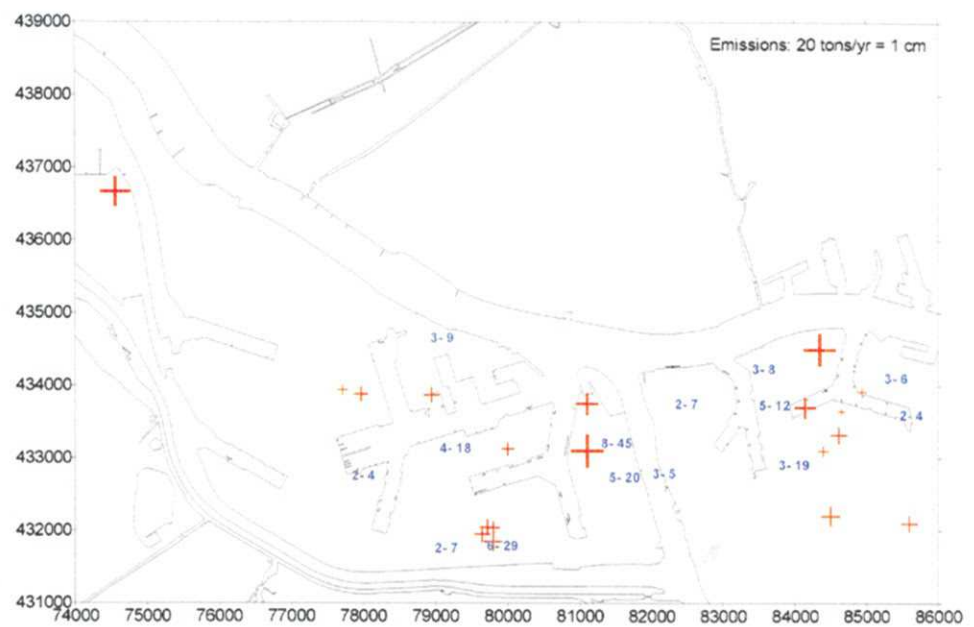the three-monthly are presented in Figure 4.10.
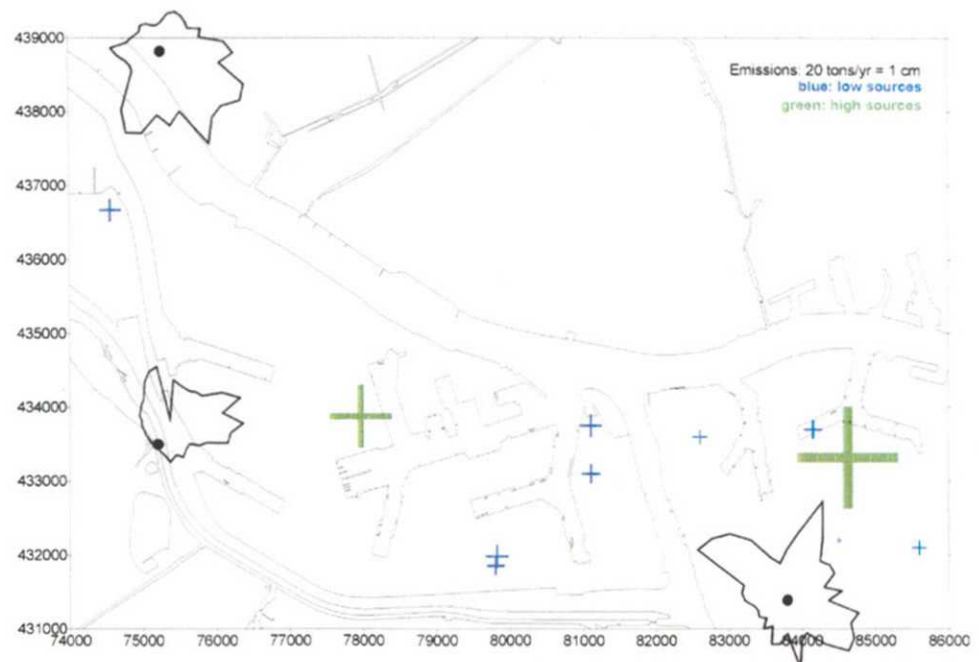
Figure 4.10   Benzene emission rates in ton/year of the emission sources in the Bot-
lek/Pernis area calculated from the results of hourly measurements, as indi-
cated by the windroses in Maassluis, Hoogvliet and Zwartewaal.

The windroses at Hoogvliet, Maassluis and Zwartewaal illustrate that air concentrations of benzene in the wind sectors representing transport of air pollution from the Botlek/Pernis area are elevated. In Table 4.6, the "default" EI emission rates and the multiplication factors of these rates as computed from the (background and traffic corrected) hourly measurement results are presented. Also, information on the emission height, as retrieved from the EI database is provided.

Table 4.5   The height of emission sources, the EI emission rates of benzene in ton/year and multiplication factors of the EI emission rates computed from hourly measurements.

source	EI Annual emission (ton/year)	active factor		height (m)
1	39	0	± 0	< 10
2	18	0	± 0	< 10
3	10	0	± 0	< 10
4	10	0	± 0	< 10
5	10	0.6	± 0.1	< 10
6	9	0	± 0	< 10
7	9	0	± 0	< 10
8	8	0.5	± 0.1	< 10
9	8	0.4	± 0.1	< 10
10	7	0.1	± 0	< 10
11	7	0.7	± 0.3	< 10
12	5	0	± 0	< 10
13	4	0	± 0	< 10
14	4	0	± 0	< 10
15	4	0	± 0	< 10
16	4	–	–	< 10
17	3	0	± 0	< 10
18	3	0	± 0.4	< 10
19	3	0	± 0	< 10
20	3	–	–	213
21	3	0	± 0	< 10
22	3	1.1	± 0.2	< 10
23	2	2.5	± 0.4	< 10
24	2	0	± 1.5	< 10
25	2	0	± 0	< 10
26	2	–	–	40
27	2	3.5	± 2.6	< 10

It is noted in Table 4.6, that for a number of sources the multiplication factor for the emission rate is calculated as zero values (sources: 1-4, 6, 7, 12-15, 17-19, 21 and 24-25). This result of the statistical analysis indicates that these sources are **not** contributing to the air concentrations of benzene at the three receptor locations. Source 22 shows factor within an order of magnitude from unity, which indicates that the emission rate is *equal* to default EI values. Sources 23 and 27 are *underestimated* by the EI, while the other sources 5 and 8-11 show values less than unity, which is an indication of *overestimation* by the EI of actual benzene emissions. Sources 16, 20 and 26 do not result in multiplication factor with adequate certainty. Hence, no information on the emission sources is collected by the measurements. It is assumed that emission by high stacks in between numerous low emissions can not be detected by the three receptor sites.

It is concluded that the measured air concentrations of benzene by hourly measurements *outside* the industrial area does not provide a monitoring instrument to control benzene emissions from on high stacks.

4.5.5   Comparison of benzene emission rates computed from *passive* and *active* sampling

In the former two sections, benzene emission rates of sources in the Botlek/Penis area have been computed both from two-weekly passive sampling and hourly active measurements. In this section, the results are compared to analyse the advantages of both methods. In Table 4.6, multiplication factors of the emission rates as assessed by both methods are summarised.

Table 4.6   *The height of emission sources, the EI emission rates of benzene in ton/year and multiplication factors of the EI emission rates computed from both passive sampling and hourly measurements.*

source	EI Annual emission (ton/year)	factor active	passive	height (m)
1	39	0.0	0.0	< 10
2	18	0.0	0.0	< 10
3	10	0.0	0.1	< 10
4	10	0.0	0.1	< 10
5	10	0.6	–	< 10
6	9	0.0	0.0	< 10
7	9	0.0	0.0	< 10
8	8	0.5	0.6	< 10
9	8	0.4	0.0	< 10
10	7	0.1	0.5	< 10
11	7	0.7	1.6	< 10
12	5	0.0	1.9	< 10
13	4	0.0	0.4	< 10
14	4	0.0	0.3	< 10
15	4	0.0	0.0	< 10
16	4	–	0.9	< 10
17	3	0.0	0.8	< 10
18	3	0.0	0.0	< 10
19	3	0.0	0.4	< 10
20	3	–	–	213
21	3	0.0	0.0	< 10
22	3	1.1	1.1	< 10
23	2	2.5	2	< 10
24	2	0.0	–	< 10
25	2	0.0	–	< 10
26	2	–	–	40
27	2	3.5	0.0	< 10

From Table 4.6 it is learned that the triangle of three sampling locations at several kilometers from the industrial area does not monitor stack emissions among low sources, while passive samplers provide more adequately emissions from lower sources (lower than 10 m), including diffuse emissions. Based upon this information, a cost-effective abatement strategy may be developed to reduce benzene (and other hydrocarbon) emissions especially from low sources. In Figure 4.11a, b and c, the ground-level iso-concentration maps of benzene are presented, as a results of emission rates computed from respectively, the EI default values, passive sampling and hourly measurements.
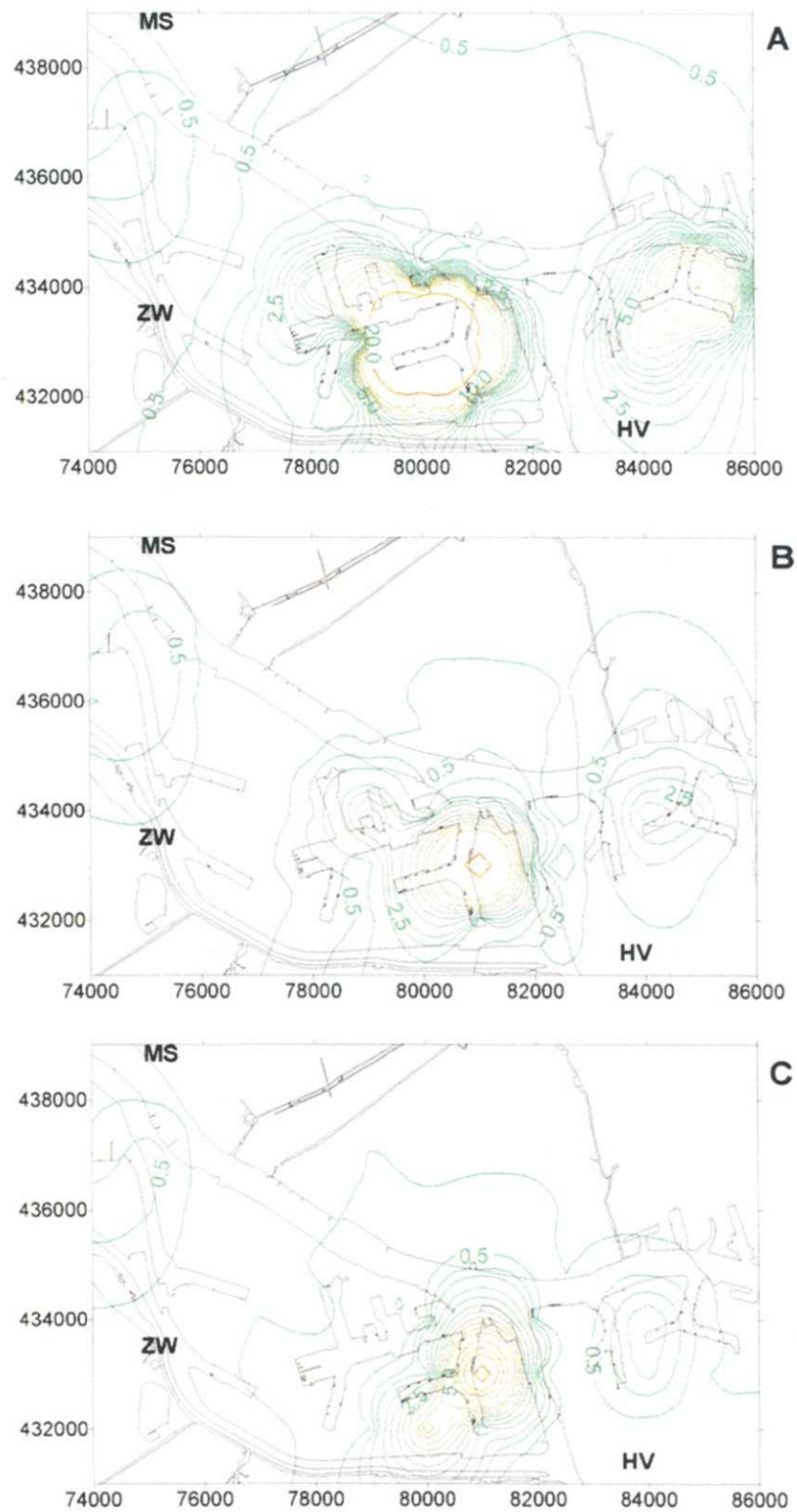
Figure 4.11   Three monthly iso-concentration map of ground-level benzene in $\mu g/m^3$ computed from EI default values (a) , passive sampling results (b) and hourly measurements results [c].

Figure 4.11 illustrates that all three methods (EI, passive sampling and direct measurements) indicate that the highest benzene ground-level concentrations are around two main emission source areas: the first at x/y co-ordinates: 80000/433000 and the second at 85000/434000. Figure 4.11c also illustrates that the benzene emissions of the high stacks do *not* result in elevated ground-level concentrations. Hence, high stacks dilute effectively gaseous pollution.

In order to assess the cost-benefits of both passive sampling and hourly measurements, a first-order costs estimate is performed:

- *passive sampling*; In the three months period, six times fourteen passive sampling periods have been performed. This totals 90 analysis of passive sampling, including six duplicates. The cost of one analysis for benzene, including the costs of a sampler is 100 ECU. Hence, for analysis the costs are 9000 ECU. Staffing inputs for the measurements concern about seven field trips (one to select locations and six to change samplers), which costs in total about 8000 ECU. So, the total costs for sampling and analysis is 17000 ECU.

- hourly measurements; In the three monthly period, benzene measurements have been implemented by three so-called "BTX" monitors. The cost of a monitor is about 25000 ECU. The cost of weather-proof housing, including power supply, air-conditioning and gases is about 35000 ECU. Hence, in total for three locations 1800000 ECU is required. A depreciation period of four years results in the costs of a three monthly campaign of about 15000 ECU. During this period, also seven field trips are envisaged to set-up and break-down the equipment and five inspection trips, which costs about 8000 ECU. So, the total costs for sampling and analysis is 23000 ECU.

This illustrates the cost-effectiveness of passive sampling, but even more important are the flexibility of the locations of passive samplers over fixed weather-proof locations and lack of problems common in field campaigns such as power failure, equipment problems and the need for chemicals.

4.5.6   Discussion and conclusions

The results of benzene demonstrate that with prior information on emission rates and locations (the so-called default EI values), a sufficient number of passive sampling locations and a triangle of up- and downwind locations with hourly measurements and application of Baysian statistics, the method provides information on *temporal fluctuations* of emission rates (in accordance to the sampling period) and the *reliability* of calculated emission rates. Both passive and active sampling give comparable results, but passive sampling *within* the industrial area details especially low sources. Passive sampling is preferred as it is a cost-effective, flexible and robust method. It is noted that even in case of a large number of emission sources (27) and a limited number of passive sampling

locations (14), the method results in adequate emission rates with emphasis on low sources.

4.6 C_2-C_5

In the next section, the methodology for "C_2-C_5" hydrocarbons is demonstrated with emphasis on ethene.

4.6.1   Factor analysis

The "C_2-C_5" concentrations at Zwartewaal have been analysed with factor analysis in order to identify source categories contributing to the air concentrations. Table 4.5 shows the results of the factor analysis. The output of factor analysis are loadings of each compound on a number of factors, as well as the correlation coefficients between the factors. A total of three factors explained more than 80% of the total variance in the data.

Table 4.7   Results of factor analysis on "C_2-C_5" concentrations measured at Zwartewaal. Only factor loadings are presented which exceed the value of 0.4.

	factor I	factor II	factor III
acetylene			0.856
ethane		0.624	
ethene		0.914	
i-butane	0.827		
i-pentane	0.935		
n-butane	0.876		
n-pentane	0.970		
propane	0.408	0.768	
propene		0.983	
Factor correlation			
factor I	1	0.334	0.311
factor II	0.334	1	0.413
factor III	0.311	0.413	1

Table 4.7 shows that factors I, II and III correlate only weakly (0.31 - 0.41) indicating an adequate distinction between source categories in the data. Factor I is characterised by high loadings of i/n-butane and i/n-pentane which is an indication for evaporation from storage tanks. Factor II shows high loadings of ethane, ethene, propane and propene, which is an indication for chemical industries in general. Factor III only presents acetylene which is an indication for traffic emissions.

Factor I: evaporation from storage tanks

Factor analysis shows that the four components i/n-butane and i/n-pentane are measured in a fixed profile. From EI data it is known that these four compounds figure prominently in the emission profile of storage tanks in the Botlek/Pernis area. In Figure 4.12 the measured concentrations of i/n-butane and i/n-pentane in Zwartewaal, as a function of winddirection are presented. This includes only hours for which the windspeed is larger than 3 m/s.
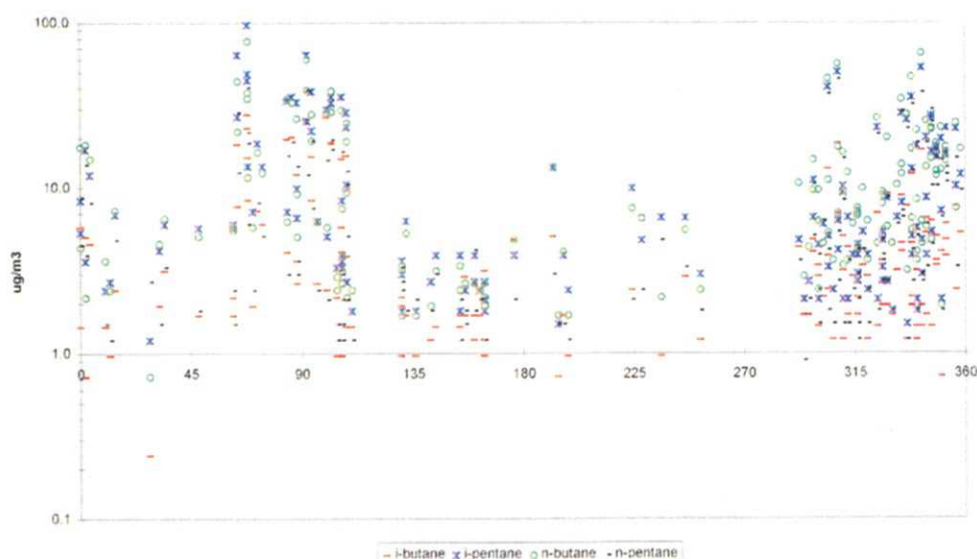
Figure 4.12   Hourly i/n-butane and i/n-pentane air concentration in µg/m3 in Zwartewaal in different windsectors and during windspeeds larger than 3 m/s.

Figure 4.12 shows two prominent peaks of i/n-butane and i/n-pentane air concentrations. High levels of i/n-butane and i/n-pentane are measured at eastern wind directions (windsector: 60-120). This points at a number of storage tanks at a distance between 2.5 and 5 km easterly from Zwartewaal *inside the Botlek/Pernis area*. High levels of i/n-butane and i/n-pentane air concentrations at northern wind directions (windsector: 300-10) identifies storage tanks between Zwartewaal and Maassluis at a distance of 3 km *outside the Botlek/Pernis area*.

There is a slight difference between the profiles from the two sectors: in the profile from the east i-pentane represents the largest fraction, whilst in the northern profile n-butane dominates. The sector-averaged profiles are shown in Table 4.8 together with the profile of gasoline evaporation from the literature.

Table 4.8   Average measured profiles for i/n-butane and i/n-pentane measured at
              Zwartewaal in easterly and northern windsectors. Also shown is the profile
              of gasoline evaporation emitted by storage tanks from literature.

	i-butane	i-pentane	n-butane	n-pentane
sector north:	0.13	0.28	0.37	0.22
sector east:	0.15	0.35	0.32	0.18
gasoline evaporation:	0.14	0.36	0.29	0.21

Table 4.8 shows that the profile from the east agrees reasonably well with the
gasoline evaporation profile, while the northern profile deviates from the latter
profile. A possible explanation for the deviating profile of the emission from
the storage tanks north of Zwartewaal may be the storage of for example
kerosine (instead of gasoline).

Factor I shows that the method is an excellent instrument to identify and
monitor emissions from storage tanks by measuring up-and down-wind VOC air
concentrations at hourly sampling periods.

Factor II: chemical industry
Factor II is characterised mainly by the compounds ethene and propene and less
by the compounds ethane and propane. Especially, ethene and propene air con-
centrations are well correlated with a coefficient of correlation of 0.87 and a
ratio of ethene to propene air concentrations of 6. Hence, factor II is well rep-
resented by ethene air concentrations, which indicates refinery processes and
chemical base industries in general. In Figure 4.13 the air concentrations of
ethene in Zwartewaal are presented. These air concentrations are corrected by
the background and traffic emissions using the Maassluis air concentrations at
relevant winddirections. An overall traffic contribution at Zwartewaal has been
estimated using the traffic profile. This contribution is found to be marginal
compared to the measured levels used in the analysis below.
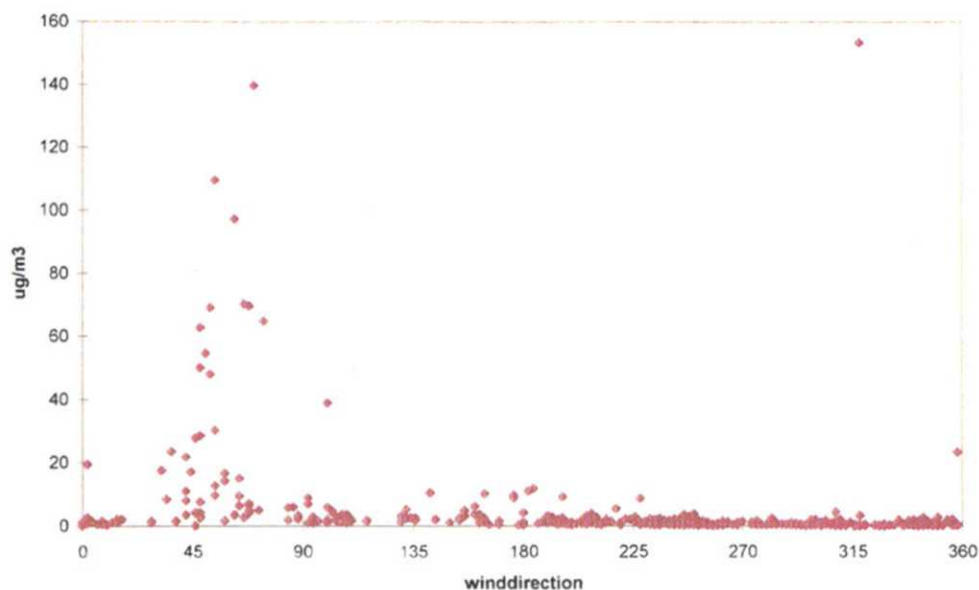
*Figure 4.13 Measured air concentrations of ethene at Zwartewaal as a function of
winddirection, including only hours for which windspeeds exceed 3 m/s.*

Figure 4.13 shows that ethene air concentrations strongly peaks during north-
easterly winds (windsector: 30-75). This indicates a (or a cluster of) ethene
source(s) north-east from Zwartewaal. Taking into account, the measured
ethene concentrations at Maasluis and Hoogvliet during the relevant winddirec-
tions (south-east for Maasluis and north-west for Hoogvliet) limits the dis-
tance of the ethene source to less than 4 km north-east from Zwartewaal. A
source at a larger distance would result in higher ethene concentrations, as cal-
culated with the dispersion model, than the ethene concentrations actual meas-
ured at Hoogvliet and Maassluis.

Inspection of provisional data of the Emission Inventory of 1996 results in a
potential ethene source north-east of Zwartewaal. The source is a chemical
plant emitting ethene from a low height. The emission is distributed over the
whole terrain of 250x250 m and yields an annual total of 7923 kg. Figure 4.14
shows the measured and calculated ("model") ethene concentrations at Zwarte-
waal for all hours for which ethene has been measured in the wind directions
from 0 - 90 degrees.
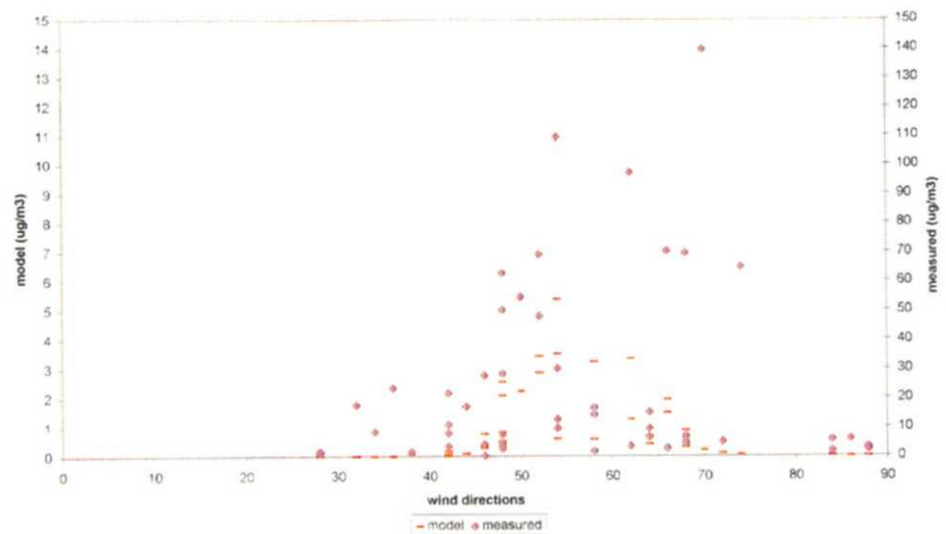
Figure 4.14   Model and measured ethene concentrations in Zwartewaal in de windsector 0- 90.

Figure 4.14 illustrates that the *calculated* concentrations based upon the default EI data are a factor 10 to 100 times smaller than the *measured* concentrations. Note the difference of a factor ten between the two vertical axes for the model calculations and the measurements! Possible explanations for the differences between the measurements and the model are:

1. the dispersion model underestimates the concentrations from a surface source;
2. the emission rate from the Emission Inventory is too low; and/or
3. an unknown ethene source.

In view of the agreement between measurements and model calculations for benzene, which was emitted mostly by surface sources, the first explanation is not likely. This leads us to the conclusion that the emission rate of the ethene source is a factor 10 to 100 times larger than the EI value or an unknown ethene source has been identified. Further information on possible new ethene related activities is required to further investigate these ethene emissions. This is beyond the scope of this project.

The example of ethene demonstrates that up- and down-wind monitoring and simple spatial regression statistics may help to identify (unknown) VOC emissions.

Factor III: traffic emissions

Factor III is characterised by a high loading of acetylene. A plot of the air concentrations of acetylene in Zwartewaal as a function of the windsectors shows that acetylene is also elevated in the same windsector as ethene. This indicates that the identified ethene source is also emitting acetylene. However, the temporal behaviour of acetylene is different from ethene which indicates the influence of another source (otherwise acetylene would have a high loading on factor II). Considering the relatively large contribution of traffic (73%) to the total emission of acetylene, as indicated in Table 3.1, suggests that traffic is the most likely source. Traffic emissions are beyond the scope of this research and therefore acetylene is not further elaborated.

Discussion and conclusions

The example of "C_2-C_5" analysis illustrates the application of factor analysis to identify various *source categories* emitting specific profiles of "C_2-C_5". Plotting air concentrations of "C_2-C_5" components which are representative for the emission profiles, as a function of the wind sectors provides information on the location of the source categories. Using EI information and air concentrations of other receptor locations in relevant wind sectors, identifies the location of the potential sources. Finally, model calculations using actual meteorological conditions and a fit with the measured air concentrations provides emission rates of specific components. A large ethene source was identified following this method which was (in 1995) not registered in the EI. Further investigation is beyond the scope of this project.

4.6.2 C_2-C_5 emission rates by FTIR measurements

The results of the VOC measurements with emphasis on "C_2-C_5 VOC" air concentration measurements obtained by FTIR remote sensing during a week within the Botlek/Pernis area are evaluated in this section. The FTIR results are presented in Table 4.9.

Table 4.9   The air concentrations on each beam position of the FTIR in the Botlek/Pernis area.

beam position	μg/m³			
	Ethane	Propane	Butane	Pentane
1				
2				
3				
4				
5				
6				
7			31	37
8	11	32	540	
9	35	129	248	
10			28	
11				
12				203
13				160
14		13		
15				
16				
17		7		
18			47	
19			188	
20			83	
21			859	

The beam positions in Table 4.9 in accordance to the four regions a to D within the Botlek/Pernis area are indicated in Figure 3.4. In addition to "C_2-C_5 hydrocarbons", also methane, benzene and hydrocarbons higher than C_6 were measured, but the results have not been indicated in Table 4.9. The detection limit of FTIR for individual compounds in ambient air is about 2 mg/m³ per meter and hence for the 200-300 meter path length applied during this campaign, the detection limit is about 5-10 μg/m³ per "C_2-C_5 hydrocarbon". As illustrated in Table 4.9 for most "C_2-C_5 VOC", the ground-level air concentrations within the Botlek/Pernis area are below these values, but especially the beam positions 7-10 in the region B (see Figure 3.4) indicate elevated ground-level "C_2-C_5 VOC" air concentrations. In the following two sections, the results for air concentrations of benzene (region A) and butane (region B) are used to illustrate the FTIR methodology to estimate VOC emissions.

benzene by FTIR

In region A at beam position 2 (see Figure 3.4), elevated ground-level benzene concentrations were measured due to benzene emissions up-wind (south) of the beam. The results are shown in Figure 4.15.
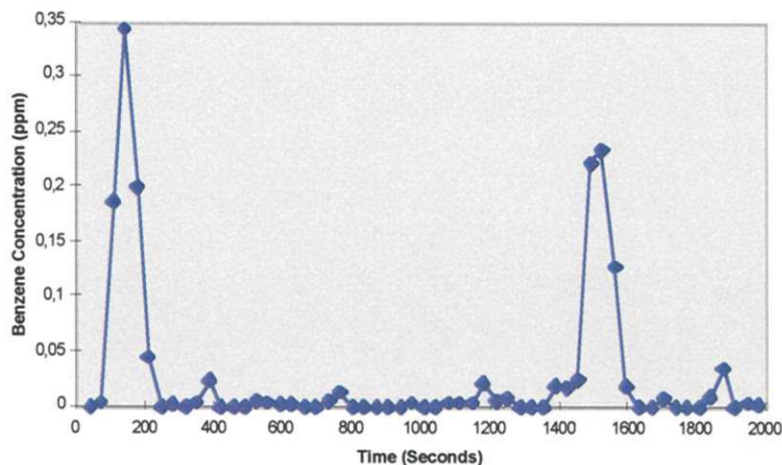
Figure 4.15   A time series of benzene concentrations measured at beam position 2 in region A of the Botlek/Pernis area.

Figure 4.15 shows that two peak concentrations of benzene occurred with a duration of about 200 seconds for each peak with a maximum concentration of about 110 $\mu g/m^3$. There was no evidence of wind direction change during the measurements which suggests that a temporal change of emission rates is the cause of the variation in benzene air concentrations. In Figure 4.16, the benzene emissions as a function of height of the benzene emission sources are presented.

Figure 4.16   Benzene emission at 1.5 m, 6.0 m and 15.0 m height in region A of the Bot-
lek/Pernis area in ton per year (tpa) and the maximum peak during the
measuring campaign in ton per year.

The benzene emissions up-wind of the beam position was calculated in the grid 640 - 880 (x-axe) and 3120 - 3360 (y-axe). Especially, in the grid cell 800 (x-axe)/ 3360 (y-axe), a benzene emission source of more than 5 ton per year is identified. Site inspection and Emission Registration provides information on storage tanks in the aforementioned grid. The FTIR results suggests that a single tank is responsible for the benzene emissions measured at beam 2.

C_2-C_5 by FTIR

The case of butane measurements in region B at beam positions 7-11 (see Figure 3.4), is used to illustrate the potential of FTIR to establish C_2-C_5 emission rates. In Figure 4.17 the calculated butane emissions in region B are shown as a function of the height of the butane emission source.
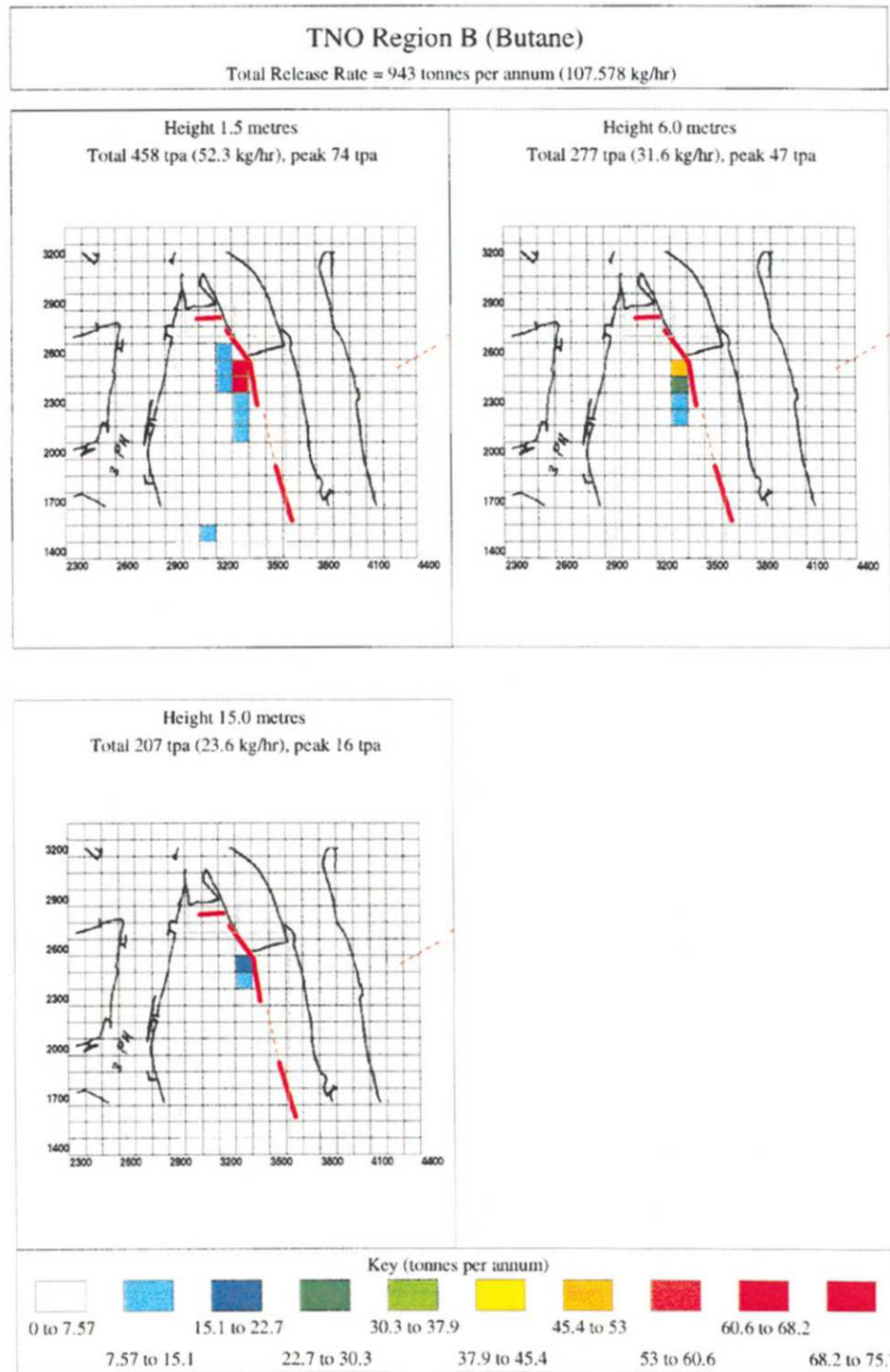
Figure 4.17   Butane emission at 1.5 m, 6.0 m and 15.0 m height in region B of the Bot-lek/Pernis area in ton per year (tpa) and the maximum peak during the measuring campaign in ton per year.

Figure 4.17 presents butane emissions up-wind of the beam positions 7-11 in the grid 2900 - 3500 (x-axe) and 1500 - 2700 (y-axe). The major source of butane emissions have been located between beams 8 and 9, on the premises of a chemical factory. The butane emissions in region B are not correlated with pentane emissions, which suggests that butane is emitted by a chemical process and not by evaporation of a storage tank of hydrocarbons. Similar to butane and benzene also for methane, ethane, propane, pentane and the sum of "C6 and higher VOC" the emission rates in the various regions A to D (see Figure 3.4) have been calculated.

Table 4.10   Emission rates of "C_1-C_6 and higher VOC" in the regions A to D in the Botlek/Pernis area.

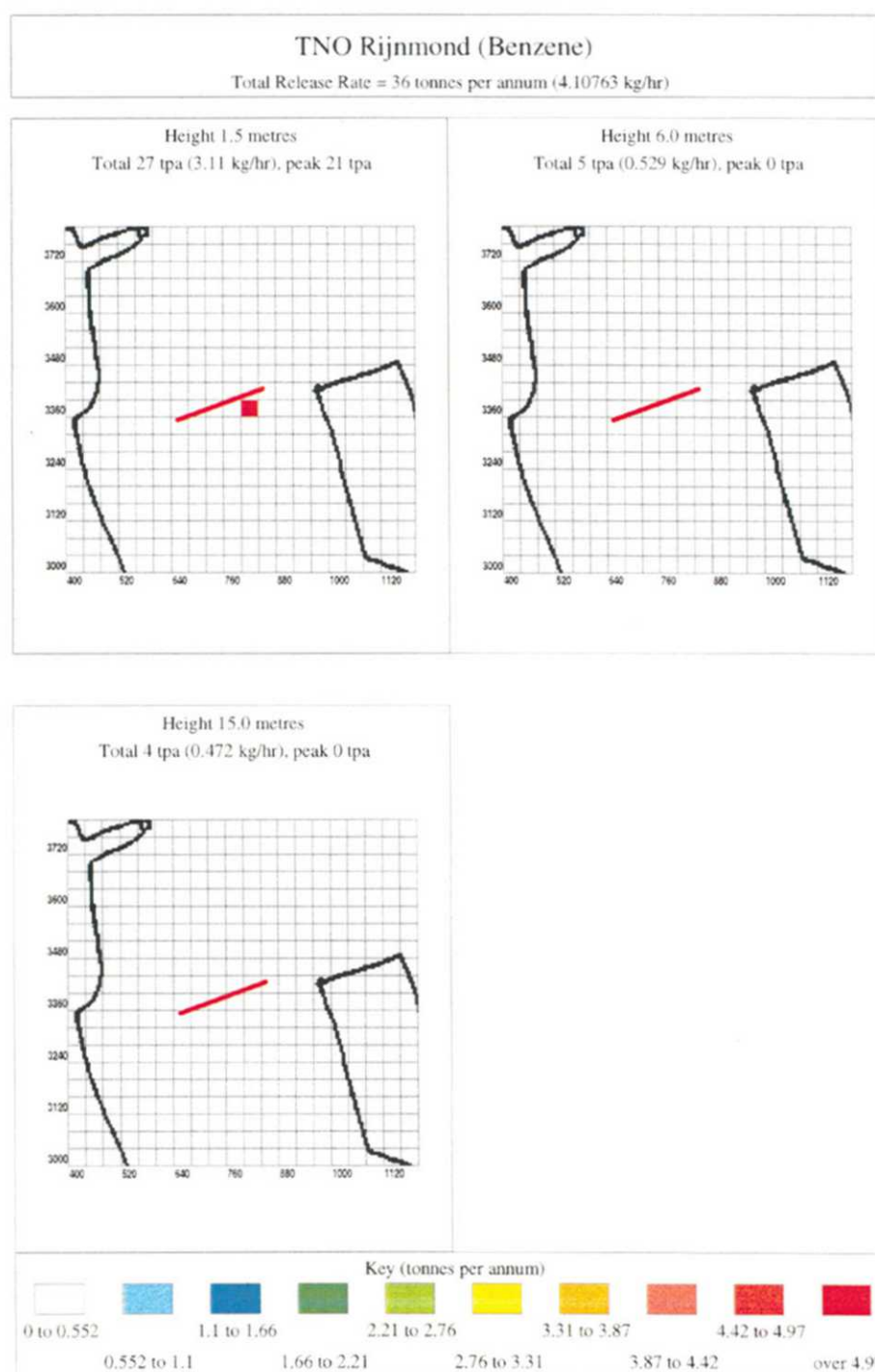| Region	Emission Rate (ton per year)					
	Methane	Ethane	Propane	Butane	Pentane	C_6 and higher
A	1100					820
B	1670	210	270	940	160	2240
C	1620					1030
D	300			70		1320

It is noted in Table 4.10 that methane has been included for information purposes as this component has only been measured by FTIR and not by the other methods in this research. The methane measurements have been corrected for "background" methane, which is about 1.2 mg/m^3, hence the emission rates in Table 4.10 are related to Botlek/Pernis emissions (leakage of natural gas?). The ER emission rates of the whole of the Botlek/Pernis area for propane and butane are respectively 320 and 2350 ton per year, which agrees reasonable with the 270 and 940 in the B-region measured with FTIR. It is noted that the sum of the emissions of methane and "C_6 and higher VOC" in region A to D are respectively 4700 and 5410 ton per year.

Discussion and conclusions

FTIR has previously mainly applied to assess VOC emissions from individual plants, where beam positions provide overlapping data and ground-level concentrations of VOC are higher than in the Botlek/Pernis area. Under the conditions of the demonstration in the Botlek/Pernis area, the degree of overlap of the beams was minimal and therefore, the results could not illustrate the full potential of the method. However, it is concluded from the results that FTIR is very well suited to identify VOC emissions from a single tank and to provide information on emission rates of methane and the sum of "C_6 and higher VOC" which was not available from the other methods applied in this research.

4.6.3 C_2-C_5 air concentrations by HAWK measurements

C_2-C_5 air concentrations were also measured by two HAWK remote sensing monitors for a period of two weeks at Zwartewaal and Maassluis. The results of the HAWK measurements showed a diurnal pattern with in- and decreasing air concentrations during respectively night and day.

The detection limit of individual "C_2-C_5 VOC" by HAWK is about 5 $\mu g/m^3$ and the relative response for methane, ethane, n-butane, n-pentane and n-hexane is respectively 0.06, 0.6, 1.2, 1.5 and 1.5. The background concentration of methane is about 1200 $\mu g/m^3$, while the sum of "C_2-C_5 VOC" air concentrations (as indicated in Annex 1) at Maassluis and Zwartewaal measured by other methods in this project are about 50 $\mu g/m^3$. Hence, the HAWK detection is dominated by ambient methane air concentrations.

From these results and the specifications of the HAWKS, it is concluded that the measured fluctuations at Maassluis and Zwartewaal reflect more a less the natural diurnal fluctuation of the background concentration of methane due to the de- and increasing mixing height. Hence, no VOC emissions from the Botlek/Pernis area could be established by the HAWK measurements. It is recommended to limit VOC emission measurements with HAWK remote sensing equipment to plant conditions, where the ratio methane/C_2-C_5 is much lower than under ambient air conditions.

5.   Conclusions and Recommendations

findings

The demonstrated methodology to assess "C_2-C_8 hydrocarbon" emissions from an industrial area is summarised by the following steps: i.) collection of prior information on emission-rates and -locations (i.e. from an Emissions Inventory database or production characteristics in an industrial area), ii.) collection of hourly-averaged meteorological data, iii.) two-weekly passive sampling *within* an industrial area for "C_6 and higher hydrocarbons" and/or hourly measurements *outside* an industrial area for "C_2-C_5 hydrocarbons" and "C_6 and higher hydrocarbons", and iv.) data analysis by spatial linear regression and Baysian statistics in combination with a short-term inverse-dispersion model.

The results of data analysis of the measuring campaign in and around the Botlek/Pernis area indicate that *styrene* emission rates of the most important sources are a factor 10 smaller than the values in the EI database of 1995; *benzene* emission rates of the 27 most important sources agree within a factor 2-4 with the EI database, with the exception of the stack sources at 40 and 213 m; and an unknown *ethene* emission source in the Botlek/Pernis area was identified. The measured two-weekly averaged emission rates of styrene and benzene show fluctuations over an order of magnitude and consequently, also ground-level air concentrations of these compounds.

reliability

The *reliability* to determine VOC emission rates by combined measurements and modelling depends on a number of factors:

- it is required that meteorological conditions during the period of air sampling are adequately determined. Atmospheric stability and wind direction are major factors contributing to the dispersion and transport of air pollutants. In this project, general meteorological conditions were measured by a meteorological station at a vicinity of 30 km from the Botlek/Pernis area, while wind direction was measured in the centre of the Botlek/Pernis area. This approach assured a relatively adequate estimate of hourly-averaged meteorological conditions;
- a second aspect is the quality of the atmospheric dispersion model. It is important to use a model in accordance to the conditions characterised by parameters as follows: i.) distance of the emission source to the sampling location, ii.) hourly-averaged air concentrations and meteorological data and iii.) information from the EI on the emission source characteristics such as stack height and plume rise. The updated National Plume model applied in this project is the "state-of -the-art" Gaussian plume model in the Netherlands for hourly dispersion modelling;
- a third aspect is the linear relation between emission and ground-level concentration of the VOC compounds, i.e. when the effects on the concentra-

tion of deposition and chemical conversion during transport from the source to the monitoring location are small. The selected "C_2-C_8 hydrocarbons" in this project comply with this condition; and

- a fourth aspect are the uncertainties in comparing EI emission rates with the computed data. The EI data are based upon *annual* emissions from 1995, while emissions calculated in the project are based upon a three-monthly campaign in 1997. In addition, the EI data address emissions based upon "routine" industrial activities, while the measurements monitor VOC emissions during actual production conditions. Based upon these considerations, it is concluded that comparison of calculated emission rates by the proposed methodology and the EI emission rates only provides a "first order" estimate about the reliability of the method.

conclusions

Taking into account the aforementioned uncertainties, it is concluded that the results presented in this report for styrene, benzene and ethene demonstrate that the method provides adequate information on the *spatial distribution* of emission sources, *chemical profiles* of emission sources, *temporal fluctuations* of emission rates, *distinction in low (diffuse) and high (stack)* emissions and the *reliability* of the calculated emission rates.

A second conclusion is that the most cost-effective and simple methodology which can be applied to assess emission rates of "C_6 and higher VOC" (including chlorinated compounds) by *low* sources is based upon passive sampling within the industrial area. For "C_2-C_5 VOC" emissions, a triangle of up- and downwind receptor locations are required based upon hourly on-line measurements and/or active sampling.

A third conclusion is that the developed method provides an important instrument for enforcement agencies to monitor actual VOC emissions from a complex industrial sources, not only on an annual but even at a two-weekly basis. This is an important aspect in order to check the effects of measures to reduce industrial VOC emissions.

A fourth conclusion concerns VOC emission measurements by the "HAWK" and "FTIR" remote sensing techniques. It is concluded that the HAWK is not an adequate technique to estimate VOC emissions from an industrial area, due to its lack of sensitivity for "C_2-C_5 hydrocarbons" as compared to methane air concentrations. Under plant conditions with a more favourable "C_2-C_5 hydrocarbons"/methane ratio, HAWK measurements is a suitable on-line detection technique, due to its simple operation as compared to automated GC. The FTIR in combination with Bayesian statistics is a promising method to determine VOC emission rates, though (due to the relatively high detection limits) the method is more adequate for on plant measurements.

Finally, it is concluded that the objectives of the project: *to develop and demonstrate a methodology to assess VOC emissions, and to estimate the contributions by various source categories in a complex industrial area based upon ground-level VOC measurements* have been achieved. Presently, there is no need for further development of the method, but there is definitely need for more practical experiences.

recommendations
It is recommended to apply the method for at least over a period of a year and to compare the results with EI emission data. Furthermore, it is recommended to apply the method for an industrial area without Emission Inventory data and finally, to apply the method within an industrial complex to monitor diffuse emissions and (if possible) in combination with the FTIR method.

6.   Dissemination activities

Two workshops have been organised in the framework of the project, the first at March 6th and the second at December 4th 1997 at TNO in Apeldoorn, the Netherlands. During the workshops, the measuring and modelling strategies as well as the results were presented to national and international experts.

In addition to both the workshops, also, at a GENEMIS meeting at October 9th 1997 in Stuttgart in the framework of the EUROTRAC programme, the project was presented to a group of European senior scientists.

In 1998, publication in environmental magazines and a scientific journal is planned to further disseminate the developed methodology. In addition, an information sheet is prepared to be submitted to relevant authorities, industrial associations and private companies.

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Annex 1   Results of the measurements

Table I.1a: Average and standard deviation of air concentrations of C2-C5 at Zwartewaal in ug/m3 at various windsectors.

windsector (degrees)	average number of measurements	C2 H2		C2 H4		C2 H6		C3 H6		C3 H8	
		average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
0	68	0,55	1,89	0,65	4,80	3,49	4,07	1,16	6,87	0,63	4,84
45	60	0,76	6,47	4,43	21,66	6,53	9,54	0,77	5,76	5,08	23,29
90	59	1,43	5,35	2,36	11,92	7,45	7,94	2,45	10,09	2,18	5,81
135	25	1,04	1,56	2,54	3,94	4,34	4,91	1,34	3,09	2,00	4,08
180	76	0,75	2,31	1,44	5,00	3,69	4,04	1,12	9,06	1,47	6,05
225	112	0,46	1,93	0,85	3,17	2,59	4,55	0,54	2,90	0,83	3,00
270	77	0,51	1,55	0,55	2,75	2,67	2,99	0,60	2,20	0,53	2,54
315	86	0,37	6,50	0,39	6,49	3,61	7,01	1,47	13,92	0,37	6,42

windsector (degrees)	average number of measurements	C4 H10 (i)		C4 H10 (n)		C5 H12 (i)		C10 H12 (n)	
		average	stdev	average	stdev	average	stdev	average	stdev
0	68	1,24	6,62	0,57	3,05	4,32	11,57	3,39	3,95
45	60	0,74	5,15	0,73	6,18	2,51	8,85	6,98	10,31
90	59	2,66	10,86	1,35	5,61	5,89	15,67	6,91	6,80
135	25	1,42	2,15	1,01	1,73	2,59	3,38	4,12	2,62
180	76	1,13	6,70	0,76	3,37	2,40	6,91	3,66	4,96
225	112	0,57	3,05	0,45	1,89	1,86	4,46	2,54	4,35
270	77	0,59	2,45	0,53	1,54	1,71	3,35	2,72	2,60
315	86	1,43	14,10	0,37	6,49	3,53	17,22	3,62	7,43

Table I.1b: Average and standard deviation of air concentrations of C2-C5 at Hoogvliet in ug/m3 at various windsectors.

windsector (degrees)	average number of measurements	C2 H2		C2 H4		C2 H6		C3 H6		C3 H8	
		average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
0	15		0,3	2,7	0,7	4,7	1,2	2,4	1,2	5,2	1,6
45	9	1,5	0,4	2,5	0,6	3,9	0,8	2,2	0,6	3,5	0,8
90	6	3,1	3,0	3,8	1,5	4,5	0,9	2,3	0,6	4,5	1,5
135	6	2,0	0,4	4,3	0,9	4,0	2,7	2,8	1,0	5,5	1,3
180	4	2,7	1,1	3,6	1,5	3,9	0,4	2,1	0,7	4,3	0,8
225	16	1,6	0,8	2,9	1,5	5,2	1,9	1,7	0,7	4,3	1,8
270	7	1,5	0,7	2,4	1,1	5,8	1,9	2,0	1,1	5,3	2,6
315	12	1,9	1,1	3,5	1,7	8,1	3,8	3,2	1,9	9,0	4,6

windsector (degrees)	average number of measurements	C4 H10 (i)		C4 H10 (n)		C5 H12 (i)	
		average	stdev	average	stdev	average	stdev
0	15	6,53	4,78	20,66	14,67	28,14	24,01
45	9	3,15	1,11	7,87	2,01	10,05	1,84
90	6	6,50	6,00	18,57	15,82	17,20	14,49
135	6	7,42	6,96	22,66	25,96	25,53	29,75
180	4	7,17	4,39	21,75	12,34	24,47	17,81
225	16	4,03	2,17	10,86	6,32	11,97	6,22
270	7	7,13	6,58	18,27	16,25	24,35	28,40
315	12	10,49	7,09	20,61	8,85	21,67	10,62

Table I.1c: Average and standard deviation of air concentrations of C2-C5 at Maassluis in ug/m3 at various windsectors.

windsector (degrees)	average number of measurements	C2 H2		C2 H4		C2 H6		C3 H6		C3 H8	
		average	stdev	average	stdev	average	stdev	average	stdev	average	stdev
0	17	1,0	0,4	1,9	0,8	3,2	1,5	1,3	0,5	2,9	1,7
45	9	1,2	0,5	2,0	0,8	5,1	4,2	1,7	0,6	3,5	2,3
90	7	1,7	0,7	2,8	1,1	4,1	2,4	1,7	0,5	3,6	1,9
135	3	1,6	0,4	3,3	0,2	3,8	2,1	5,6	4,9	7,2	2,9
180	9	1,5	0,8	2,5	1,6	3,0	2,1	3,5	2,7	4,5	2,6
225	16	1,8	1,1	2,8	1,4	5,0	4,0	1,9	0,7	6,8	2,7
270	8	1,2	0,6	2,0	0,6	3,9	1,3	1,7	1,0	5,4	2,6
315	14	1,4	0,8	2,2	1,1	4,1	2,1	1,6	0,7	5,8	5,6

windsector (degrees)	average number of measurements	C4 H10 (i)		C4 H10 (n)		C5 H12 (i)	
		average	stdev	average	stdev	average	stdev
0	17	2,59	2,00	7,25	6,14	10,84	6,85
45	9	1,97	1,99	5,19	4,18	8,63	5,11
90	7	2,64	2,62	8,88	9,99	14,26	11,66
135	3	3,81	0,37	9,51	1,32	13,98	2,09
180	9	3,60	2,66	10,17	9,48	13,71	12,45
225	16	5,63	2,79	16,16	8,65	21,27	11,15
270	8	3,67	3,27	11,80	12,31	16,39	14,18
315	14	2,86	1,77	8,33	4,71	11,17	6,67

Table I.2a: Average and standard deviation of air concentrations of BTX at Hoogvliet in ug/m3 at various windsectors.

windsector (degrees)	average number of measurements	benzene average	stdev	toluene average	stdev	ethyl benzene average	stdev	m-xylene average	stdev
0	236	4,1	3,6	9,1	6,0	2,3	1,4	4,0	2,7
45	111	3,2	2,9	7,9	6,7	2,5	2,1	4,3	4,0
90	35	3,2	3,4	8,0	2,3	2,3	2,0	3,9	3,8
135	32	2,4	1,4	6,1	4,0	1,7	1,1	2,8	2,2
180	115	2,7	2,2	7,2	6,4	2,0	1,6	3,0	2,8
225	164	2,1	2,5	4,7	3,6	1,3	1,0	2,0	1,7
270	226	2,6	2,1	5,0	3,6	1,4	1,1	2,1	1,8
315	236	4,2	3,3	6,1	3,9	1,8	1,1	2,6	1,6

windsector (degrees)	average number of measurements	p-xylene average	stdev	o-xylene average	stdev	styrene average	stdev
0	236	1,7	1,7	2,2	1,4	0,9	2,3
45	111	2,4	1,4	2,4	2,1	4,0	6,1
90	35	2,1	2,0	2,2	2,1	0,4	0,6
135	32	1,2	1,2	1,6	1,2	0,4	0,3
180	115	1,5	1,4	1,7	1,5	0,4	0,4
225	164	0,9	0,9	1,2	1,0	0,4	0,3
270	226	1,0	1,0	1,3	1,1	0,7	1,1
315	236	1,4	1,0	1,5	0,9	0,6	0,8

Table I.2b: Average and standard deviation of air concentrations of BTX at Maassluis in ug/m3 at various windsectors.

windsector (degrees)	average number of measurements	benzene		toluene		ethyl benzene		m-xylene	
		average	stdev	average	stdev	average	stdev	average	stdev
0	502	2,0	1,9	4,5	4,4	2,1	3,8	2,6	2,9
45	279	1,8	1,3	4,2	3,1	2,0	1,3	2,3	1,9
90	118	2,4	1,4	6,6	4,3	2,4	1,3	3,8	2,7
135	51	4,3	3,4	8,6	5,9	3,0	1,6	5,0	4,0
180	269	3,7	2,2	6,2	4,5	3,4	2,5	3,4	2,8
225	264	3,3	3,8	4,8	4,1	2,1	1,6	2,7	2,8
270	250	2,4	6,0	4,1	3,3	1,7	0,7	2,3	1,8
315	315	1,5	0,9	3,4	2,8	1,6	0,8	2,1	1,5

windsector (degrees)	average number of measurements	p-xylene		o-xylene		styrene	
		average	stdev	average	stdev	average	stdev
0	502	1,1	1,3	1,4	1,4	0,8	0,6
45	279	0,9	0,7	1,2	0,9	0,5	0,3
90	118	1,4	1,0	1,9	1,3	0,6	0,4
135	51	1,9	1,3	2,3	1,6	0,6	0,3
180	269	2,3	1,6	1,9	1,9	0,7	0,7
225	264	1,9	1,9	1,5	1,6	0,6	0,4
270	250	1,5	1,6	1,2	0,9	0,6	0,4
315	315	0,8	0,6	1,1	0,8	0,5	0,3

Table II.3A: Average and standard deviation of VOC air concentrations in ug/m3 measured during six periods in the Botlek/Pernis area with passive samplers.

sampler code	benzene average	stdev	toluene average	stdev	ethylbenzene average	stdev	p+m-xylene average	stdev	o-xylene average	stdev	styrene average	stdev
P1	3,1	0,9	3,8	1,1	1,3	0,8	3,0	1,3	0,8	0,3	0,0	0,1
P2	5,4	2,5	6,7	2,7	2,2	0,9	8,6	2,8	1,8	0,9	0,5	0,2
P3	4,5	2,2	6,4	2,5	1,6	0,9	6,6	5,5	2,2	1,4	0,2	0,3
P4	7,6	5,2	9,2	3,4	3,9	1,7	6,8	2,6	2,6	1,5	3,3	2,3
P5	13,0	8,5	21,6	8,4	2,6	0,9	8,2	2,4	2,6	0,7	0,4	0,4
P6	18,8	16,2	16,0	3,5	4,8	1,6	9,1	1,1	3,7	1,2	2,4	0,9
P7	9,8	5,6	10,6	1,2	3,6	1,1	7,1	1,3	2,6	0,9	1,1	0,5
P8	4,1	1,8	10,1	8,8	1,8	0,5	3,9	1,1	1,7	0,4	0,4	0,4
P9	3,9	0,9	10,0	2,9	1,5	0,3	3,2	0,8	1,2	0,4	0,4	0,3
P10	4,4	1,8	10,9	4,5	2,4	0,9	5,8	2,8	2,3	0,9	1,3	0,6
P11	7,9	2,6	20,3	4,6	3,9	1,2	9,6	2,9	3,7	0,9	1,2	0,4
P12	8,0	6,0	15,7	10,2	3,2	1,8	7,8	4,3	3,0	1,3	1,0	0,6
P13	3,8	1,3	9,1	3,5	2,3	0,6	5,6	1,5	2,1	0,7	2,1	0,9
P14	3,1	0,8	7,0	1,6	2,2	0,4	4,7	0,8	2,0	0,4	12,6	9,0

sampler code	124-trimethylbenzene average	stdev	n-decane average	stdev	n-undecane average	stdev	cyclohexane average	stdev	methylcyclohexane average	stdev	hexane average	stdev
P1	0,5	0,4	0,4	0,4	0,4	0,3	3,6	2,4	3,1	4,1	2,3	1,4
P2	1,3	0,8	0,7	0,2	0,8	0,5	4,0	2,5	1,5	0,9	4,6	2,5
P3	0,8	0,2	0,5	0,2	0,5	0,4	2,9	2,8	1,6	0,5	2,9	1,0
P4	1,4	0,4	1,7	0,9	1,5	0,7	20,3	20,6	2,9	0,9	5,8	1,9
P5	1,1	0,3	0,6	0,3	0,5	0,4	10,2	10,7	2,5	0,8	4,9	1,3
P6	2,6	0,4	2,0	0,4	1,8	0,4	4,9	1,6	4,6	1,3	11,3	2,6
P7	1,7	0,2	1,3	0,3	1,4	0,3	2,9	1,5	2,8	0,8	7,3	1,5
P8	1,6	0,5	1,1	0,5	1,4	0,6	2,1	0,5	2,1	0,6	8,2	5,0
P9	1,2	0,4	0,9	0,3	1,3	0,4	1,5	0,3	1,8	0,4	6,0	1,6
P10	1,6	0,5	1,0	0,4	1,0	0,3	1,6	0,4	2,5	0,8	7,7	2,5
P11	2,4	0,7	1,6	0,7	1,7	0,6	1,8	0,3	3,8	1,1	10,8	3,0
P12	1,9	0,7	1,2	0,4	1,3	0,4	2,0	1,0	6,0	4,4	12,0	6,3
P13	2,1	0,5	2,4	1,4	5,0	3,9	1,8	0,3	2,7	0,8	7,4	2,6
P14	1,4	0,3	0,9	0,1	1,1	0,3	2,0	1,0	2,3	1,0	6,4	3,7

TableII.3b: Air concentrations in ug/m3 during three periods at Zwartewaal, Maassluis and Hoogvliet measured with passive samplers.

location	period	benzene	toluene	ethyl-benzene	p+m-xylene	o-xylene	styrene	n-decane	n-un-decane	cyclo-hexane	methyl-cyclohex.	hexane
Zwartewaal	16/4-14/5											
	14/5-10/6	1,2	3,4	0,5	1,4	0,6	0,0	0,4	0,3	0,8	0,7	2,2
	10/6-9/7	0,6	1,7	0,3	0,6	0,2	0,0	0,3	0,0	0,6	0,4	1,3
Maassluis	16/4-14/5		3,7	1,0	4,5	0,7	0,3	0,3	0,4	2,7	1,8	5,6
	14/5-10/6	1,8	4,7	0,9	2,7	1,1	0,0	0,3	0,3	0,9	1,0	3,2
	10/6-9/7	1,3	3,0	0,6	1,6	0,7	0,0	0,0	0,0	0,9	0,7	2,3
Hoogvliet	16/4-14/5	3,6	7,3	1,3	3,8	1,4	0,5	0,5	0,5	1,0	1,5	4,8
	14/5-10/6	2,5	5,9	1,2	3,1	1,2	0,7	0,5	0,4	1,1	1,3	4,5
	10/6-9/7	2,5	5,5	1,0	2,7	1,0	0,4	0,3	0,4	1,1	1,1	3,8

Table II.4: Average and standard deviation of VOC air concentrations in ug/m3 in Hoogvliet, Maassluis and Zwartewaal measured by tenax sampling tubes from 10 AM till 16 PM in the period mid April till mid July.

component	Hoogvliet	(n=69)	Maassluis	(n=70)	Zwartewa	(n=57)
	average	st.dev.	average	st.dev.	average	st.dev.
hexane	3,6	5,4	4,9	5,0	3,6	4,1
trichloromethane	0,1	0,0	0,1	0,0	0,0	0,0
methylcyclopentane	1,4	2,3	1,8	1,7	0,8	1,1
2,4-dimethylpentane	0,3	0,4	0,3	0,3	0,1	0,1
1,1,1-trichloroethane	0,2	0,2	1,5	4,4	0,3	0,3
benzene	2,5	2,8	2,5	2,5	1,4	1,9
tetrachloromethane	0,5	0,5	0,5	0,4	0,5	0,3
2-methylhexane	1,4	1,9	1,3	1,1	0,5	0,7
3-methylhexane	1,0	1,3	0,9	0,8	0,3	0,4
2,2,4-trimethylpentane	1,2	1,4	1,0	1,0	0,3	0,5
trichloro-ethene	0,1	0,1	0,3	0,6	0,1	0,1
n-heptane	1,6	2,0	1,8	1,7	1,0	1,0
methylcyclohexane	0,6	0,9	1,0	1,3	0,3	0,6
2,5-dimethylhexane	0,2	0,2	0,2	0,2	0,0	0,0
2,4-dimethylhexane	0,3	0,3	0,3	0,3	0,1	0,1
toluene	10,2	14,3	6,2	6,6	2,8	4,7
3-methylheptane	0,3	0,4	0,3	0,3	0,1	0,1
n-oktane	0,6	0,7	0,7	0,6	0,5	0,8
tetrachloorethene	0,3	0,3	0,1	0,2	0,1	0,1
ethylbenzene	1,7	2,1	1,7	1,6	0,6	0,7
p,m-xylene	4,5	5,5	4,0	4,1	1,2	1,2
styrene	0,6	1,0	0,2	0,2	0,1	0,2
o-xylene	1,8	2,1	1,8	1,6	0,5	0,5
n-nonane	1,0	1,0	1,2	1,1	1,0	0,9
iso-propylbenzene	0,2	0,3	0,1	0,2	0,1	0,0
n-propylbenzene	0,4	0,4	0,4	0,3	0,1	0,1
3-ethyltoluene	1,7	1,9	1,4	1,1	0,4	0,4
4-ethyltoluene	0,6	0,7	0,6	0,5	0,1	0,1
1,3,5-trimethylbenzene	0,3	0,4	0,3	0,3	0,1	0,1
2-ethyltoluene	0,4	0,5	0,4	0,4	0,1	0,2
1,2,4-trimethylbenzene	1,8	2,4	1,5	1,3	0,3	0,4
n-decane	0,9	1,1	1,0	1,0	0,8	1,1
1,2,3-trimethylbenzene	0,3	0,3	0,3	0,4	0,1	0,1
n-undecane	0,7	0,8	0,7	1,1	0,4	0,4
naftalene	0,2	0,3	0,1	0,2	0,1	0,0
n-dodecane	0,3	0,4	0,2	0,3	0,4	0,7