Effects of Sea Water Scrubbing

Final report

Marc Hufnagl, Research Centre Terramare, Schleusenstrasse 1, 26382 Wilhelmshaven, Germany

Prof. Dr. Gerd Liebezeit, Research Centre Terramare, Schleusenstrasse 1, 26382 Wilhelmshaven, Germany

Dr. Brigitte Behrends, School of Marine Science and Technology, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

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Abbreviations

Anth	Anthracene
BaA	Benz[*a*]anthracene
Chry	Chrysene
DCM	Dichloromethane
DIN	Dissolved inorganic nitrogen
DIN	Deutsche Industrie Norm
DOM	Dissolved organic material
DOP	Dissolved organic phosphorus
EPA	Environmental Protection Agency
Flu	Fluoranthene
FMN	Flavin mononucleotid
GC-FID	Gas-Chromatography Flame Ionisation Detector
GC-MS	Gas-Chromatography Mass Spectroscopy
IAPSO	International Association for Physical Science of the Ocean
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IDL	Instrument Detection Limit
InjSTD	Injection Standard
ISTD	Internal Standard
LOD	Limit of Detection
PAH	Polycyclic Aromatic Hydrocarbon
Phe	Phenanthrene
PIP	Particulate inorganic phosphorus
PoK	“Pride of Kent” the ferry on which the seawater scrubber is installed
POP	particulate organic phosphorus
Pyr	Pyrene
RDP	Reactive dissolved phosphorus
SI	Shell Index
SIM	Single Ion Monitoring
SPE	Solid Phase Extraction
SQU	Squalane (used as Injection Standard)
SWS	Seawater scrubber
TBrB	1,2,4,5-Tetrabromobenzene (used as Injection Standard)
TDP	Total dissolved phosphorus
TCHL	Total chlorophyll
TPP	total particulate phosphorus

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1 Project description

In May 2003 BP-Marine in co-operation with P&O Ferries built a flue gas desulphurisation system prototype manufactured by DME Canada into a channel ferry (“Pride of Kent”), operating between Dover (UK) and Calais (France). To fulfil the legal requirements of Marpol Annex VI this seawater scrubber should remove mainly SO_2 from the exhaust gases. In addition other harmful emissions and noise should also be reduced. The analysis of the liquid effluents as well as their influence on the marine environment, especially that of the ports, was carried out by Terramare Research Centre in Wilhelmshaven, Germany.

2 Summary

Within this project the effects of a seawater scrubber onto the environment were analysed. During five sampling campaigns in 2004 the main focus was laid on pH, nutrients, temperature, trace metals, polycyclic aromatic hydrocarbons (PAH) and plankton. Additionally one accumulation and two toxicity tests were performed. For the observation of a whole annual cycle, samples were taken in February, March, July, September and November inside the harbours of Dover and Calais and on board the “Pride of Kent” (PoK). Inside the ferry’s seawater scrubber system very low pH values and high PAH concentrations, even in the outlet, were measured. Sulphate and nitrate concentrations were also higher on board than in samples from the harbour environment. Metal contents, especially of iron and vanadium, which were leached from the steel, could also be detected in high amounts inside the system. A decrease of the pH inside the ports or close to the ferry was never observed. Only in one case the temperature was slightly higher in front of the effluent outlet. Although PAH concentrations were high in the effluent, no increased concentrations were observed inside the harbours or in front of the ship. Significant contents of heavy metals or eutrophication effects were also not detected. In summary, no negative influence of the scrubbing system on the port environments was observed.

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3 Introduction

Marine diesel engines are among the most fuel-efficient combustion sources for moving goods [Corbett and Koehler, 2003]. Nevertheless they also contribute significantly to air pollution (e.g. Capaldo et al., 1999; Streets et al., 2000). In the past regulations have been passed which dealt especially with the SO_2 emissions from land based combustion sources. Examples for these are the European Union Directives 1999/30/EC, 2001/81/EC and 1999/32/EC. But since there were no sulphur limits for marine heavy fuel oils, these now contain a high amount of sulphur relative to other fuels.

Burning of fuel gives rise to SO_2 and SO_x formation, which damages sensitive ecosystems and buildings. In the marine boundary layer especially ships contribute to a high input [Capaldo et al., 1999]. Another by-product of fossil fuel burning is the emission of NO_x. In marine regions with high traffic, ships may increase NO_x levels significantly. Both, SO_x and NO_x and additionally soot particles not only cause environmental damage but also health damage. NO_x for example increases, as well as volatile organic compounds, the formation of ground level ozone. If the O_3 concentration is elevated above national standard levels (US EPA: 0.12 ppm) it may cause lung and respiratory disorders. Additionally some materials like rubber, nylon, plastic, dyes and paints might be damaged by ozone. A study revealed that children from rural Ontario communities show a decrease in lung function and higher susceptibility for bronchitis [Mac Phail et al.]. Also plants, e.g. agricultural crops and trees, are negatively affected by increased ozone concentrations [WHO 1997].

SO_x and also NO_x are also responsible for the formation of acid rain. Acid rain describes a phenomenon which has been known since the early 1970s and which has caused a number of problems [Driscoll et al. 2001]. For example in soils cations like Mg^{2+} and Ca^{2+} are leached whereas sulphur and nitrogen concentrations increase. Additionally the harmful dissolved inorganic Al^{3+} increases which influences the water uptake capacity of trees. Moreover tree mortality has risen because calcium is leached from the needles of gymnosperms thereby increasing their susceptibility to freezing injury. In lakes the acid neutralising capacity is still decreasing resulting in an increasing acidification and aluminium contents resulting in a decreasing species diversity. Model calculations show that only with a marked reduction in sulphur emissions a measurable chemical improvement of the affected ecosystems is possible. In many areas, mainly close to the major shipping routes and harbours, sulphur emissions from ships may equal natural sources. The European Environment Agency estimates that shipborne contributions from international shipping in the North Sea and north-east Atlantic Ocean to total European acidifying emissions may about double by 2010 as a result of increasing marine traffic (Fig. 1, EEA, 2000).

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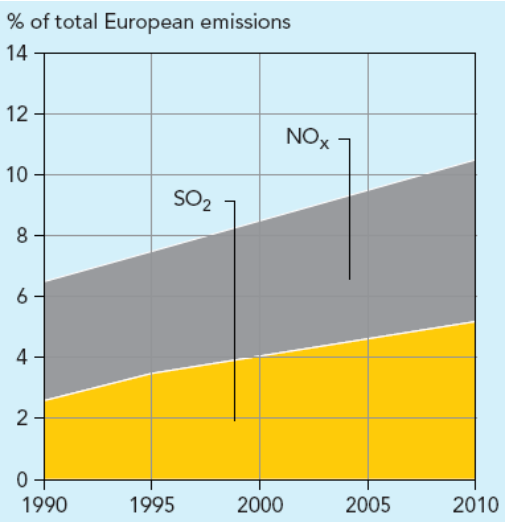

Fig. 1 Estimates of shipborne contributions to total European NO_x and SO_2 emissions 1990 – 2010 (EEA, 2000)

To regulate especially this anthropogenic impact of SO_x, an international instrument on air pollution from ships was developed by the Maritime Organisation in 1997: Marpol Annex VI. Marpol Annex VI was ratified in May 2004 by 15 flag states representing at least 50 % of the gross tonnage of the world merchant shipping. It will come into force in May 2005. Furthermore, it has to be taken into account that the cost of limiting the sulphur content of marine bunker oils in the North and Baltic Seas to 1.5 % (the maximum value accepted by MARPOL) has been estimated at about 87 million € per year. Equivalent reductions in total emissions from landbased sources (such as power stations) would cost about 1,150 million € per year.

Among other regulations, Marpol Annex VI will introduce a 4.5 % sulphur limit for marine fuels and a 1.5 % sulphur limit for marine fuels burned in the so-called SO_x emission control areas. Burning of fuel with higher sulphur content is only allowed when technologies are used which reduce the atmospheric emissions from ships to less than 6 g kWh^{-1} (as SO_2 mass). Fluegas desulphurisation processes like for examples seawater scrubbing are one possible technology [Tokerud, 1989]. These systems are no new technology but have been used world wide since 1930 in coal power plants located close to the sea (cf. Behrends and Liebezeit, 2003). Their main task is to reduce the sulphur dioxide (SO_2) and other sulphur oxides (SO_x) contents in the exhaust gases which are produced from burning high sulphur content coal. Additionally nitrogen oxides (NO_x) and particulates are removed partially from the exhaust gas. The reduction and the theoretical effects of a seawater scrubber system are described in detail in Behrends and Liebezeit [2003]. Thereafter SO_x and NO_x dissolve within the scrubber effluent and form nitric, nitrous and sulphuric acids. These might, on one hand, reduce the pH of the receiving waters and, on the other hand, might due to the input of nitrate lead to eutrophication.

Besides gaseous components soot is also formed, especially during incomplete combustion. This is mainly made up of elemental carbon with the particular features of a large surface area and a hydrophobic character. Nonpolar substances immediately adsorb onto these particles and are then transported with the soot from the combustion source. Polycyclic aromatic hydrocarbons (PAHs constitute a major group of these substances. While the low molecular weight PAHs such as

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naphthalene (two rings) or phenanthrene and anthracene (three rings) are mainly found unbound in the gaseous phase already a major fraction of the four-ring members like pyrene, chrysene and benz[*a*]anthracene are bound to these carbon particles.

The formation of PAHs and a major part of all reactions that take place during combustion have been presented by Duran et al. 2004. In addition to this pyrolytic formation there are several other PAH sources such as petrogenic oil formation processes. In this case these compounds are created during the slow maturation of organic material. With regard to the sources of PAHs there is a broad spectrum of possibilities for them to enter the environment: industrial wastewater, street dust runoff discharges, deposition of fossil fuel combustion particles, carbonized coal product spills, forest and grass fires, volcanic particles, oil spills or natural oil seeps [Witt and Trost, 1999; Lake et al. 1979, Lee et al. 1981]. Usually PAHs are occurring in a complex mixture of isomers and alkylated isomers [Wise et al., 1993]. Low molecular weight PAHs with two or three rings are present normally in dissolved form in water or gaseous in atmosphere. The higher the molecular weight the more hydrophobic they behave and the more they are bound to particles [Ahrens, Depree, 2004, Pleil et al., 2004, Doong and Lin, 2004]. Therefore highest PAH concentrations are to be found in sediments [Neff 1979; Pearlman et al., 1984].

Taking all sources in consideration it is not surprising that PAHs have not only been detected in sediments but also in the atmosphere, water and soils all over the world [Fung et al. 2004; Soclo et al. 2000; Potrykus et al. 2003, Prevedouros et al. 2003]. Because some of them are toxic [Bispo et al. 1999; El-Alawi et al., 2001], some inhibit plant growth [Sudhakar Babu et al. 2001, Marwood et al. 2001] and some are carcinogenic and mutagenic [ATSDR 1997] their distribution and behaviour in the environment has been subject to several studies.

When PAHs are introduced into the environment several reactions may occur. Besides to the described adsorption to particles and also dissolved organic material (DOM) [Sun et al., 2003], photooxidation is one of the major reactions. In most cases these photooxidized forms are even more toxic than the parent compounds [Sudhakar Babu et al., 2001; El Alawi et al., 2001; McConkey et al., 1997; Ankley et al. 1994]. For example the photooxidized form of anthracene inhibits the photosynthetic electron transport system [Huang et al., 1997]

Biological degradation, mainly due to microbial action [Weissenfels et al., 1992; Heitkamp and Cerniglia 1989], is another important factor in alteration and reduction. In this case it has to be taken into consideration, that degradation of combustion derived PAHs is expected to be slower for PAHs from petrogenic origin [Yunker et al., 1996; Mc Groddy and Farrington, 1995; Gustafsson et al., 1997]: In addition, the PAH concentrations [Yuan et al. 2001], the amount of total organic carbon [Hinga 2003; Webster et al., 2001] and the particle size [Schnelle-Kreis et al. 1999] seem to play a role in removing and degradation of PAHs from or in the water.

Additionally it has to be taken into account that because of the different sources of these PAHs, they show a distinct seasonal variability [Prevedouros et al., 2004] and also degradation might show seasonality [Pohlman et al. 2002]. These changes concern mainly combustion-derived PAHs. During

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wintertime when there is lot of wood and oil burning, environmental concentrations rise. In some regions forest fires in summer might also influence the seasonality.

The determination of the origin of PAHs is normally performed by the aid of different indices [Soclo et al., 2000; Potrykus et al., 2003, Lake et al., 1979; see below]. All in all about 600 PAH-structures [NIST 1997] have been classified and 16 of them have been defined by the United States Environmental Protection agency (US-EPA) to be environmentally relevant [US-EPA 610]. These are also the most common and best examined PAHs in the literature.

During the present study the impact of a Seawater Srubber (SWS) to reduce atmospheric emissions was examined. The ship which was equipped with this technology was the "Pride of Kent", a ferry operating between the harbours of Dover and Calais. The main focus of the survey was the harbours and the seawater within the system of the SWS. Five samplings were performed, one sampling while the SWS was not in use (11.02.2004) and four when the SWS was partially in use (March, July, September and November), which means that only the seawater scrubbers for the auxiliary engines were working.

Because both ports are influenced by tidal currents, the pH and the salinity showed a high natural variability. In front of the outlet of the seawater scrubber no decrease in pH could be detected, but effluent water was about 0.4 to 1.8 pH units lower than the inflow and the water within the harbour. An effect on temperature could only be determined during the sampling in July and September. Determined metal concentrations inside the harbour were mostly within the range of the used Atlantic water salinity standard. The comparison between the SWS-inlet and the SWS-outlet water did only indicate a rise of the zinc concentration which might haven been an effect of the sampling. Inside the system iron and vanadium were increased but most of it was amassed inside the settling tank.

Within the harbours a seasonal variability of PAHs was determined with generally higher concentrations in the winter, early spring and late autumn. Comparing the seawater inlet and outlet samples, PAH-concentrations in the outlet were about two orders of magnitude higher than in the inlet.

Sulphate and nitrate were only increased inside the seawater scrubber but not inside the ports. The toxicity tests did not clearly reveal an increased toxicity.

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4 Material and Methods

4.1 pH - buffer capacity of natural seawater

The aim of this test was to estimate the buffer capacity of seawater and the time necessary to reach pH-equilibrium after acid addition. The results could aid to predict the influence of the Ecosilencer impact.

Five different natural sea- and brackish water samples (Jade Bay, Wilhelmshaven, Germany; Ems River, Papenburg, Germany; Odense harbour, Denmark; Dover harbour, England; Calais harbour, France). The different seawater properties are listed in Table 1.

Table 1: Properties of the different river- and seawater samples used for the assays

origin	salinity [ppt]	pH	sampling temperature [°C]	test temperature [°C]
Nassau harbour, Jade Bay, Wilhelmshaven, Germany	30	8,0	3	22,5
Meyer Werft, Ems River, Papenburg, Germany	0,3	7,71	3,1	22,6
Lindoe, Odense, Denmark	21,4	7,97	3,4	20,1
Calais harbour, France	18,3	7,81	7,3	22,4
Dover harbour, England	34,3	7,86	7,4	22,4

500 mL seawater each were acidified with a mixture of HNO_3 and H_2SO_4 (1 : 1.48, v:v) to a final pH of 4.0. The mixing ratio of 1 to 1.48 was chosen because of the expected composition of the SWS Ecosilencer effluent (sulphur content in fuel = 3.5 % and four main engines and two generators running at 85 % MCR). The pH-value of pH 4 was chosen because of the worst case estimated pH of the SWS Ecosilencer and cooling water mixture effluent discharges. The acidified water was then mixed with the untreated seawater in different combinations (Table 2).

Table 2: Compositions of mixtures for pH buffer capacity test. (Mixtures in italics were not performed for every assay)

acidified seawater (pH 4) [mL]	natural seawater (about pH 8) [mL]	stirring speed [rpm]
50	450	250
100	400	250
150	350	250
200	300	250
250	250	250
250	250	250
300	200	250
350	150	250
400	100	250
450	50	250
250	250	0
1000	*1000*	*250*
500	*500*	*250*
250	*250*	*1000*

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After mixing the natural and the acidified samples, the pH was measured in regular intervals until no significant change in pH could be observed any more. Normally the test was stopped after three days. The pH for the different fractions was plotted against time and the pH in equilibrium was plotted against the percentage of pH 4 seawater in mixture and analysed.

4.2 Polycyclic Aromatic Hydrocarbons

Several tests were performed to establish the best method for the extraction of PAHs on the basis of the highest recovery rate. In the past liquid-liquid extraction was the commonly used technique to extract PAHs from aqueous solutions, but as this method is cumbersome, labour intensive, expensive and not environment-friendly due to its large solvent consumption, a less expensive and easier method was developed. Solid phase extraction (SPE) was considered to be the best method, especially as this method is favourably reported in literature [Crozier et al., 2001; Titato and Lanças, 2000; Garcia-Falcon et al. 2004] and different applications are available [Agilent Technologies; Macherey Nagel]. Therefore different Solid Phase Extraction sorbents, different sample preparations and different solvents were tested. For a comparison of the results the traditional liquid-liquid extraction (LLE) was also applied. In a series of assays the following topics were investigated:

- influence of SPE-sorbent
- influence of elution solvent
- influence of acetone addition before extraction
- recoveries for Dover and Calais waters
- incubation time of internal standard mix (fractionation of particulate and soluble PAH fractions)
- recovery rate in artificial seawater for liquid-liquid-extraction (LLE) with n-hexane

For statistical reliability at least 3 parallel experiments were performed for every test. In every experiment 500 mL of the matrix were spiked with 1 mL of a 100 µg L^{-1} PAH mixture in acetone (Sigma-Aldrich Chemie GmbH, Taufkirchen Germany) containing acenaphthylene, anthracene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*g*)perylene, benzo(*a*)pyrene, chrysene, dibenzo(*ah*)anthracene, fluorene, indeno(1,2,3-*cd*)pyrene, phenanthrene and pyrene. The final concentration was 200 ng PAH L^{-1}. Additionally 1 mL of a 100 µl L^{-1} Internal PAH Standard Mix solution in acetone was added (Dr. Ehrenstorfer GmbH, Augsburg, Germany) containing acenaphthene-D10, chrysene-D12, perylene-D12 and phenanthrene-D10. The first three tests which are mentioned above were performed in artificial seawater [RiPSUa et al. 1979] produced with deionised water, the remaining tests with natural seawater.

The SPE-cartridges were conditioned with 5 mL Methanol and flushed with about 100 mL deionised water. Thereafter 500 mL sample were aspirated slowly over the SPE sorbent. For extraction 2 + 3 mL

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dichloromethane (DCM) were used. An aliquot of 1000 µL from the resulting 5 mL extract was transferred into a 2 mL amber glass-vial and 100 µl of a 10 µg mL^{-1} TBrB were added as injection standard (InjSTD). The aliquot was analysed by gas chromatography/mass spectrometry (GC-MS; GC: HP 6890, MS: HP MSD 5973, Software: Chemstation G1701 CA) in Single Ion Monitoring (SIM; see Table 10).

Recoveries were determined by calculating the ratio of the measured PAH concentration and the concentration added to the matrix. The means and the standard deviations were calculated. In the following part the different assays are described in detail.

1. Influence of SPE-sorbent

Three different SPE-sorbents were used, all manufactured by Macherey-Nagel GmbH & Co KG, Düren, Germany.

- Chromabond EASY: a bifunctional modified polystyrene divinylbenzene copolymer phase (specific surface 650 - 700 $m^2 g^{-1}$, particle size 80 µm, pore size 50 Ångstrom, pH-range 1-14).
- Chromabond C18 ec: an octadecyl silica endcapped sorbent (base material silica, pore size 60 Å, particle size 45 µm for C18 ec, 100 µm for C18 ec f (fast flow), specific surface 500 $m^2 g^{-1}$, pH stability 2 - 8, endcapped, carbon content 14 %).
- Chromabond C18 PAH: an octadecyl silica phase for PAH analysis (60 Å, particle size 45 µm, specific surface 500 $m^2 g^{-1}$, pH stability 2 - 8).

Experiments were performed using artificial seawater.

2. Influence of Elution Solvent

SPE-cartridges filled with Chromabond C18 ec were used for extraction, two different elution solvents were tested:

- dichloromethane
- n-hexane

Experiments were performed using artificial seawater.

3. Influence of Acetone Addition before Extraction

The extraction was performed using Chromabond C18 ec and DCM as elution solvent. During these assays three different amounts of acetone were added to the sample before extraction.

- 2 mL acetone (0.2 %)
- 5 mL acetone (1 %)
- 10 mL acetone (2 %)

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The matrix was artificial seawater.

4. Recovery rates in Dover and Calais harbour waters

As natural seawater taken from Dover and Calais harbours was already contaminated with PAHs, another recovery experiment than that described above had to be executed. In this case three samples of 500 mL Dover (11.02.04, station 7) and Calais (11.02.04, station 2) seawater were filled into round flasks and spiked with 1 mL of a 100 ng mL^{-1} standard and internal standard solution. These samples were then extracted using SPE-C18 ec and DCM as elution solvent. Three additional 500 mL samples from each harbour were spiked only with the internal standard. The recoveries are then calculated by difference (see eq. 1).

$$RR = \frac{\frac{PA_s}{PA_{InjST}} \cdot \frac{1}{Sl_{Cal}} - \frac{PA_{BS}}{PA_{InjST}} \cdot \frac{1}{St_{Cal}}}{C_{spike}} \cdot 100 \qquad (1)$$

PA_s	= peak area of spiked sample
PA_{InjSTD}	= peak area of Injection Standard
Sl_{Cal}	= slope of calibration line
PA_{BS}	= peak area of unspiked blank sample
C_{spike}	= concentration of PAH spike

6. Incubation of Internal Standard Mix (Fractionation of Particulate and Soluble Fractions)

For this experiment ten subsamples of 0.5 L each, taken from a 20 L sample (24.3.2004, station 6: Dover, “Prince of Whales Pier”) were filled into 1 L amber glass bottles, acidified with 2.5 mL 50 % HCl and mixed with 0.5 mL 3 % sodium thiosulphate. Additionally the samples were spiked with 1 mL of a 100 µg L^{-1} PAH-mix and an equally concentrated ISTD Mix, closed and fixed on an orbital shaker. Two subsamples made up one group and were extracted after 1 h, 2 h, 4 h, 8 h and 16 h. Then the recoveries and the percentages of the soluble and the particulate fraction were determined. This protocol was also used for the determination of the method repeatability and for the calculation of the accuracy of the method.

7. Liquid-Liquid-Extraction

As liquid-liquid-extraction (LLE) was for long time the standard method to extract PAH from water, this test was performed as reference. For extraction 500 mL artificial seawater were spiked with 1 mL 100 µg L^{-1} PAH-Mix and 1 mL 100 µg L^{-1} ISTD, acidified with 2.5 mL HCl (50%) and filled into a 1 L separation funnel. The PAHs were then extracted with n-hexane (20 mL, 10 mL, 10 mL). All extracts

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were combined, reduced in a rotary evaporator to dryness, taken up in 1 mL DCM and, after addition of InjSTD, analysed by GC MS.

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5 Material and Methods: Determination of environmental parameters and pollutants

5.1 Sampling points, Sampling, Transport and Storage

5.1.1 Sampling in February and March

Samples were taken at nine different station inside the harbours of Dover (Fig. 3 and Table 3) and Calais and at two (11.2.04) and twelve (24.3.04) places, respectively, inside the engine room of the “Pride of Kent” during her operation inside the harbours and on the shipping route between Dover and Calais (Fig. 2).

Fig. 2: Geographical position of Dover and Calais and route of the “Pride of Kent” in the Channel

As the Ecosilencer was not operative during the first sampling on 11.2.2004, only two samples were taken from the seawater scrubber system: one from the inlet and one from the outlet. The samples shown in Fig. 3 (left) were also taken from the seawater inlet. While the ship was entering the harbours of Dover and Calais, samples were taken from the inlet and outlet. In the Channel additional samples were taken at the points listed in Table 5 after some time of operation at normal load.

For the first sampling cleaned 2 L polyethylene flasks were used and rinsed with sample water before filling. For the second sampling, the PAH-samples were stored in 1 L amber glass bottles (baked out at 250 °C for 24 h and rinsed with 5 % HCl). Each one was filled with 1 L of sample and after that 5 mL 50 % HCl and 1 mL 3 % sodium thiosulphate were added to deactivate free chlorine and to prevent samples from microbial degradation. For nutrient and metal samples 1 L polyethylene flasks treated as the other polyethylene flasks mentioned before were used.

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Table 3: Sampling points in Dover 11.02.2004 and 24.03.2004-05-28

11.2.2004	
sampling point	description
7	harbour entrance
8	middle port
9	Quay 4

23/24.03.2004	
sampling point	description
5	Churchill Hotel Beach
6	Prince of Wales Pier
7	back of “Pride of Kent”
8	middle of “Pride of Kent”
9	front of “Pride of Kent”

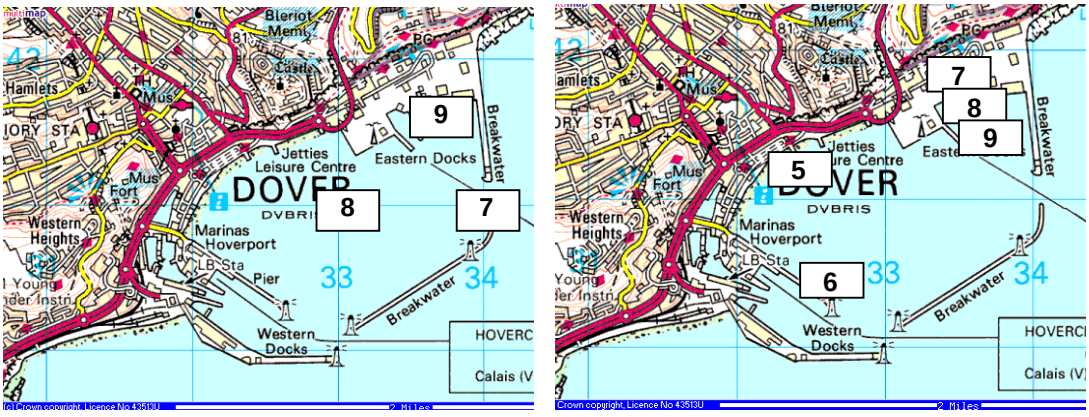


Fig. 3: Dover harbour sampling points (left: 11.2.2004, right: 24.3.2004)

Table 4: Sampling points in Calais

Sampling point	Description
Cal 1	Quai en eau profonde
Cal 2	Quai de service
Cal 3	Quai de la Loire
Cal 4	Jetee Ouest

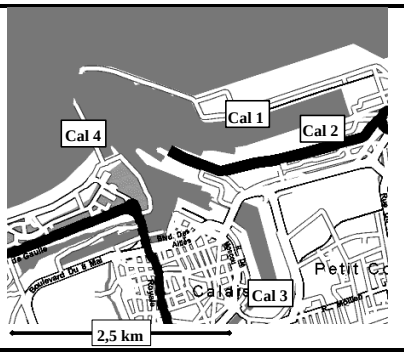
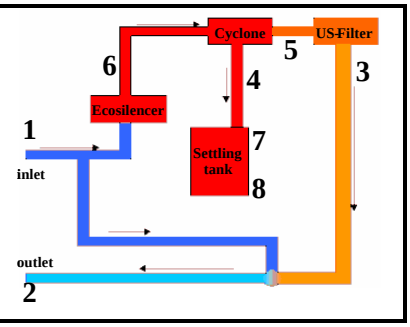


Table 5: Sampling points on board „Pride of kent“

Sampling point	Description
1	seawater inlet
2	diluted overboard discharge
3	outlet from US filter
4	dirty water to settling tank
5	inlet to US filter
6	water return from Ecosilencer
7	top of settling tank
8	bottom of settling tank



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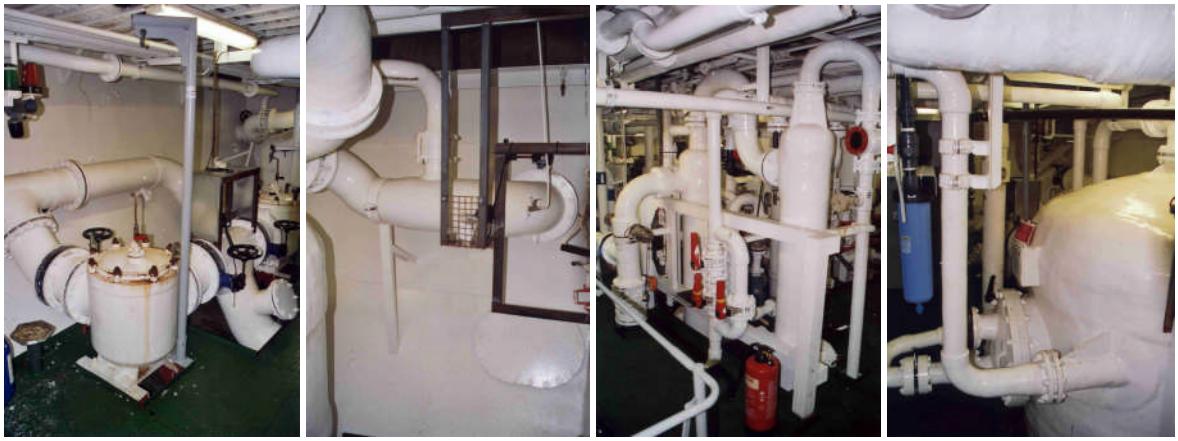

Fig. 4: Photographs of the seawater scrubber sampling points inside the “Pride of Kent”. L.: Point 1 seawater scrubber inlet. M.l.: Point 2 seawater scrubber outlet. M.r.: Point 3 and 5: outlet and inlet of US filter, top of cyclones. R.: Point 4, 7 and 8: tube going to the settling tank and top and bottom of sampling tank.

Inside the harbours 50 mL water samples for plankton determination were taken as well. These were mixed with 10 drops “Lugol’s solution” (20 g KJ, 20 g J_2, 200 mL deionised water, 20 mL acetic acid).

All bottles were transported in cooling boxes directly to the laboratory (max. 30 h), where they were stored, with exception of the plankton samples, deep frozen at -18°C until further treatment or extraction. The plankton samples were allowed to settle and the sample was analysed under an inverted microscope.

5.1.2 Sampling in July, September and November

As for the samplings in July, September and November two small boats were available. The sampling points changed and samples were also taken inside the harbours and within a transect from the outlet of the seawater scrubber towards the entrance of the harbours. The sampling points, the description and coordinates are given in Table 6, Table 7 and Table 9. In Table 9 the sampling times are also given. The sampling points SD1, SD2, SC1, SC2 and SCH1 to SCH8 refer to the sampling points of the seawater scrubber inside the “Pride of Kent”, where SD are the seawater scrubber samples taken in Dover, SC are the samples taken in Calais and SCH are the samples taken during the Channel crossing. Hih and low water times and flow for all samplings are shown in Table 8. As the “Pride of Kent” did not berth at the predicted quay during the sampling in September the point C 0 was not taken at the same place as C 5 but at a parallel quay.

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Table 6: Sampling points in Calais for the samplings in July, September and November

Sampling point	Description
Cal 1	Quai en eau profonde
Cal 2	Quai de service
Cal 3	Quai de la Loire
Cal 4	Jetee Ouest
C 0	before arrival of “PoK”
C 5	5 m from the outlet
C 50	50 m from the outlet
C 350	350 m from the outlet
C 700	700 m from the outlet

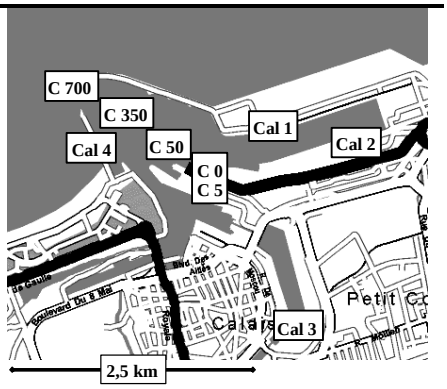

Table 7: Sampling points in Dover for the samplings in July, September and November

Sampling point	Description
Dov 1	eastern entrance
Dov 2	western entrance
Dov 3	middle port
Dov 4	close to Prince of Wales pier
D 0	before arrival of “PoK”
D 5	5 m from the outlet
D 50	50 m from the outlet
D 350	350 m from the outlet
D 700	700 m from the outlet

Table 8: High and low water times (*http://www.mobilegeographics.com*)

sampling	port	flow	low water	high water
February	Calais	11.2.04 3:44	11.2.04 10:45	11.2.04 16:07
	Dover	11.2.04 15:37	11.2.04 22:37	12.2.04 2:56
March	Calais	23.3.04 14:21	23.3.04 21:14	24.3.04 2:36
	Dover	24.3.04 0:04	24.3.04 7:04	24.3.04 12:23
July	Calais	13.7.04 10:50	13.7.04 17:35	
	Dover	13.7.04 9:09	13.7.04 16:11	
September	Calais	8.9.04 8:06	8.9.04 14:32	
	Dover	7.9.04 4:29	7.9.04 11:07	7.9.04 17:01
November	Calais	17.11.04 3:27	17.11.04 10:37	17.11.04 15:52
	Dover	16.11.04 12:33	16.11.04 19:48	

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Table 9: Coordinates of sampling points and time and date for samplings

Point	coord. N	coord. E	July	September	November
Cal 1	50° 58.161'	1° 51.491'	13.7.04 08:40	8.9.04 8:50	17.11.04 10:30
Cal 2	50° 58.180'	1° 52.042'	13.7.04 09:00	8.9.04 9:05	17.11.04 10:00
Cal 3	50° 57.385'	1° 51.562'	13.7.04 09:40	8.9.04 8:30	17.11.04 09:40
Cal 4	50° 58.010	1° 50.582	13.7.04 10:00	8.9.04 8:15	17.11.04 09:30
C 0	50° 58.052'	1° 51,382'	-	8.9.04 11:15	17.11.04 11:00
C 5	50° 58.044'	1° 50.927'	13.7.04 11:50	8.9.04 11:45	17.11.04 11:40
C 50	50° 58.079'	1° 50.846'	13.7.04 12:00	8.9.04 12:00	17.11.04 11:50
C 350	50° 58.153'	1° 50 634'	13.7.04 12:10	8.9.04 12:05	17.11.04 11:55
C 700	50° 58.311'	1° 50.457'	13.7.04 12:30	8.9.04 12:10	17.11.04 12:00
Dov 1	51° 07.109'	1° 20.459'	14.7.04 13:45	7.9.04 14:45	16.11.04 12:35
Dov 2	51° 06.914'	1° 19.749'	14.7.04 13:50	7.9.04 15:05	16.11.04 13:00
Dov 3	51° 07.100'	1° 19.854'	14.7.04 14:00	7.9.04 15:10	16.11.04 13:05
Dov 4	51° 07.149'	1° 19.327'	14.7.04 14:05	7.9.04 15:17	16.11.04 13:10
D 0	51° 07.584'	1° 20.406'	14.7.04 12:50		16.11.04 13:15
D 5	51° 07.570'	1° 20.361'	14.7.04 13:05	7.9.04 14:10	16.11.04 13:20
D 50	51° 07.526'	1° 20.387'	14.7.04 13:15	7.9.04 14:25	16.11.04 13:30
D 350	51° 07.411'	1° 20.500'	14.7.04 13:20	7.9.04 14:35	16.11.04 13:25
D 700	51° 07.292'	1° 20.589'	14.7.04 13:30	7.9.04 14:40	16.11.04 13:35
SD1	-	-	14.7.04 18:00	7.9.04 19:30	16.11.04 18:15
SD2	-	-	14.7.04 18:00	7.9.04 19:30	16.11.04 18:15
SCH1	-	-	14.7.04 18:30	7.9.04 20:00	16.11.04 18:50
SCH2	-	-	14.7.04 18:30	7.9.04 20:00	16.11.04 18:50
SCH3	-	-	14.7.04 18:55	7.9.04 20:10	16.11.04 18:50
SCH4	-	-	-	7.9.04 20:10	16.11.04 18:55
SCH5	-	-	14.7.04 19:10	7.9.04 20:15	16.11.04 18:00
SCH6	-	-	14.7.04 19:15	7.9.04 20:15	16.11.04 18:55
SCH7			-	7.9.04 20:20	-
SCH8	-	-	-		16.11.04 19:00
SC1	-	-	14.7.04 19:25	7.9.04 20:55	16.11.04 19:40
SC2	-	-	14.7.04 19:25	7.9.04 20:55	16.11.04 19:40

5.2 Temperature, pH, Salinity, Oxygen

pH-values were measured directly after sampling using a pH-Meter (WTW pH 320/WTW-SenTix 81) calibrated with two different buffer solutions (pH 7.00 and pH 4.01, Mettler-Toledo GmbH, Analytical, Schwerzenbach, Switzerland). Salinity, conductivity and temperature were determined electronically (WTW Cond 315i, Weilheim, Germany) as well.

Oxygen during the first sampling was determined by using a Winkler titration Kit (Merck, Germany). During the second sampling (24.3.04) an oxygen electrode was used (Hach LDO HQ 10, range 0-20 mg L^{-1}, Düsseldorf, Germany).

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5.3 Metals and sulphate

Metals were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Pre-treatment included acidification (5 % HNO_3) and filtration (Syrfil Mixed Cellulose Ester Filter, ∅ 25mm, 0.22 µm MF, Whatman, Maidstone, England; Norm Jet syringe, Tuttlingen, Germany). For determination mainly elements which are included in the ships processes were chosen. These include the transition metals vanadium, chromium, manganese, iron, cobalt, nickel, copper zinc and molybdenum. Additionally the earth metals barium, lithium, strontium, calcium, potassium, magnesium and the sulphate contents were measured. All samples were analysed by the working group “Inorganic Geochemistry” at the Institute for Chemistry and Biology of the Sea (ICBM) at Oldenburg University, Germany.

5.4 Polycyclic Aromatic Hydrocarbons (PAH)

5.4.1 Calibration, determination of accuracy, Carry-over

As the 16 EPA PAHs are the most widespread and commonly determined PAHs, these compounds were also chosen for determination during this work. A composition of the names, synonyms and major physical properties is shown in Table 11.

Table 10: Groups of PAHs defined for GC-MS SIM-method

group	Ret. time	Compound	MS mass
1	-	naphthalene	128
2	12.52	acenaphthylene	152
2	13.06	acenaphthene	154
2	12.96	acenaphtene-D10	164
3	14.80	fluorene	166
3	17.14	1,2,4,5-tetrabromobenzene	393.7
4	18,11	phenanthrene-D10	190
4	18.16	phenanthrene	178
4	18.32	anthracene	178
5	22.49	fluoranthene	202
5	23.19	pyrene	202
5	27.41	benzo[*a*]anthracene	228
5	27.52	chrysene-D12	240
5	27.96	chrysene	228
6	31.16	benzo[*b*]fluoranthene	252
6		benzo[*k*]fluoranthene	252
6	32.10	benzo[*a*]pyrene	252
6	32.33	perylene	264
7	35.23	dibenz[*a,h*]anthracene	278
7	35.37	indeno (*1,2,3,c,d*) pyrene	276
7	36.07	benzo[*ghi*]perylene	276

Calibration was performed by diluting a 500 mg L^{-1} PAH Mix (Sigma-Aldrich Chemie GmbH, Taufkirchen Germany) to concentrations in a range from 1 to 1000 ng mL^{-1} three times. From every dilution of the standard 1 mL was filled into an amber glass GC-vial and 50 µL of a 10 µg mL^{-1} of

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1,2,4,5-tetrabromobenzene (TBrB) and 50 µL of a 10 µg mL^{-1} squalane solution were added as injection standards (InjSTD). For the samples that have been taken during the fourth, fifth and sixth sampling squalane was not used as injection standard. The calibration standards were prepared for each chromatographic run and measured randomLy distributed over each analysis sequence. For linear regression between concentrations and peak areas in relation to InjSTD the statistic program Systat 8.0 was used (command file see appendix).

For determination of the linear range of the GC, a calibration series using nine concentrations in the range from 2.5 ng mL^{-1} to 1000 ng mL^{-1} was analysed. The linearity was then determined by linear and nonlinear regression of the calibration series with the nine different dilution steps. For linear regression the function

$$y = a \cdot x + b \qquad (2)$$

and for nonlinear regression the function

$$y = a + b \cdot x + c \cdot x^2 \qquad (3)$$

were fitted to the data. With these the value $\hat{y}$ could be calculated, which in the best case should be the same value as the concentration y of the standard. In the next step the residual-standard-deviation was calculated according to

$$s_{y_linear} = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}\left(y_i - \hat{y}_i\right)^2} \qquad (4)$$

$$s_{y_nonlinear} = \sqrt{\frac{1}{N-3}\sum_{i=1}^{N}\left(y_i - \hat{y}_i\right)^2} \qquad (5)$$

where N is the number of dilution steps, y the employed concentration and $\hat{y}$ the concentration calculated with the linear and nonlinear functions, respectively. From these values the difference DS^2 can be calculated according to

$$DS^2 = \left(N-2\right)\cdot s^2_{y_linear} - \left(N-3\right)\cdot s^2_{y_nonlinear} \qquad (6)$$

With this value the examination variable EV as

$$EV = \frac{DS^2}{s^2_{y_nonlinear}} \qquad (7)$$

was determined and compared to F (P=099%, $f_1 = 1$, $f_2 = N\text{-}3$) from a F-table. If EV was smaller or equal F the nonlinear function was not significantly better than the linear function. If this was not the case, the highest concentration was taken out of the calculation, a new function was calculated and EV was calculated again.

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Accuracy of the GC was determined by measuring the 25 ng mL^{-1} and 500 ng mL^{-1} concentrations eight times. To check for carry over, solvent blanks (DCM) were analysed distributed randomLy over the chromatographic run.

The limit of detection (LOD) was determined as three times the standard deviation (IUPAC criterion) of the 25 ng mL^{-1} concentration.

These tests were performed for the analyses with the split splitless injector and also for the samples analysed with the cold injections system.

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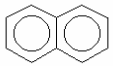
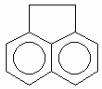
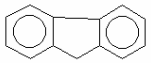
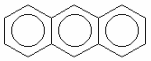
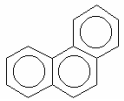
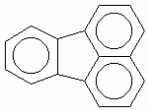
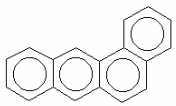
Table 11: Structures and major physical properties of the 16 EPA-PAHs

PAHs **EPA**	Name and Synonyms	Form.	CAS	Log K_{OW} (Exp./Calc.) [1]	T_{boil} [°C] [2]	T_{fus} [°C] [2]	Density [g cm^{-3}] at 20°C [3]	Vapour pressure [Pa] [4]	Solub. H_2O [mg/l] [4]	Molec. weight	Risk phrases	Safety phrases	hazard symbol
	**naphthalene**	$C_{10}H_8$	91-20-3	3,33 / 3,17	217,0	80,2	-	1.0x102	31	128,17	20,21, 22,36, 37,38, 43,45	16,26, 36,37, 39,45	T
	acenaphthylene 1,2-dihydroacenaphthylene 1,8-dihydroacenapthalin 1,8-ethylenenapthalene 1,2-dihydroacenaphthylene	$C_{12}H_8$	208-96-8	3,94 / 3,94	280,2	89,6 - 93,4	-	9.0x10-1	16	152,19	22, 36, 37, 38	26, 36, 37, 39	Xn
	**acenaphthene,** cyclopenta[d,e]naphthalene paranaphthalene	$C_{12}H_{10}$	83-32-9	3,92 / 4,15	279,2	94	1.225	3.0x10-1	3.8	154,21	36, 37, 38	26, 36	Xi
	**fluorene** ortho-biphenylene methane diphenylenemethane 2,2-methylene biphenyl 2.3-benzidene	$C_{13}H_{10}$	86-73-7	4,18 / 4,02	294,2 - 298,2	115	-	9.0x10-2	1.9	166,22	-	-	Xn
	**anthracene** anthracin green oil	$C_{14}H_{10}$	120-12-7	4,46 / 4,35	340	217	-	1.0x10-3	0.045	178,23	20, 21, 22, 36, 37, 38, 42,43	26, 36	Xn
	**phenanthrene** phenantrin	$C_{14}H_{10}$	85-01-8	4,45 / 4,35	328,15 - 340,15	99	0.980 at 4 °C	2.0x10-2	1.1	178,23	20, 21, 22, 36, 37, 38, 40	26, 27, 36, 37, 39, 45	Xn
	**fluoranthene** 1.2-[1,8-Naphthylene]-benzene 1.2-benzacenaphthene 1.2-[1.8- naphthalenediyl]benzene benzo[j,k]fluorene	$C_{16}H_{10}$	206-44-0	5,16 / 4,93	-	108 - 113	-	1.2x10-3	0.26	202,25	22, 36, 37, 38, 40	-	Xn
	pyrene benzo[d,e,f]phenanthrene 8-pyrene	$C_{16}H_{10}$	129-00-0	4,88 / 4,93	-	151	1.271 at 23 °C	6.0x10-4	0.13	202,25	26, 36, 37, 38	-	Xn
	**benzo[*a*]anthracene** BA;benz[*a*]anthracene 1,2-benzanthracene benzo[*b*]phenanthrene 2,3-phenanthrene 2,3-benzophenanthrene tetraphene, benzo[e]fluoranthene	$C_{18}H_{12}$	56-55-3	5,76 / 5,52	437,8	159	1.274 at 20 °C	2.8x10-5	0.011	228,29	45, 50, 53	45, 53, 60, 61	T N

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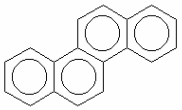
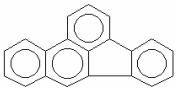
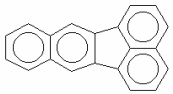
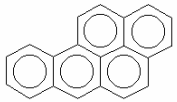
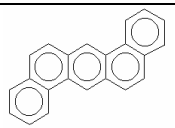
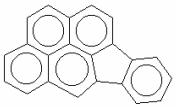
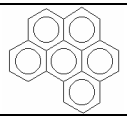
	**chrysene** 1.2-benzophenanthrene benzo[*a*]-phenanthrene 1,2benzphenanthrene benz[*a*]phenanthrene 1,2,5,6-dibenzonaphthalene	$C_{18}H_{12}$	218-01-9	5,81 / 5,52	448,2	254,35 - 258,4	-	5.7x10-7	0.006	228,29	20, 21, 22, 45, 46	3, 7, 9, 36, 37, 39, 45	T
	**benzo[*b*]fluoranthene** 3,4-Benz[e]acephenanthrylene 2,3-benzfluoranthene 3,4-benzfluoranthene 2,3benzofluoranthene 3,4-benzofluoranthene benzo[e]fluoranthene	$C_{20}H_{12}$	205-99-2	5,78 / 6,11	-	-	-	-	0.0015	252,31	45, 50, 53	45, 53, 60, 61	T N
	**benzo[*k*]fluoranthene** 8.9-benzfluoranthene 8.9-benzofluoranthene 11.12benzofluoranthene 2,3,1.8-binaphthylene dibenzo[b,j,k]fluorine	$C_{20}H_{12}$	207-08-9	6,11 / 6,11	480	217	-	5.2x10-8	0.0008	252,31	45	45, 53	Xn
	**benzo[*a*]pyrene** benzo[d,e,f]chrysene 3-4 benzopyrene 3,4-benzpyrene benz[*a*]pyrene;BP	$C_{20}H_{12}$	50-32-8	6,13 / 6,11	495,2	177	1.351	7.0x10-7	0.0038	252,31	45, 46, 50, 53, 60, 61	45, 53, 60, 61	T
	**dibenz[*a,h*]anthracene** DB[*a,h*]A DBA 1,2:5,6 dibenz[*a*]anthracene	$C_{22}H_{14}$	53-70-3	-- / 6,70	524,2	260,15 - 271,2	1.282	3.7x10-10	0.0006	278,35			
	**indeno (1,2,3,c,d) pyrene** indenopyrene IP;orthophenylenepyrene 1,10-ortho-phenylene]pyrene 1,10-[1,2-phenylene]pyrene 2,3-ortho-phenylenepyrene	$C_{22}H_{12}$	193-39-5	6,63 / 6,70	-	162 - 163	-	-	0.00019	276,33	-	-	Xn
	**benzo[*ghi*]perylene** 1,12-benzoperylene	$C_{22}H_{12}$	191-24-2	6,80* / 6,70	-	280	-	1.4x10-8	0.00026	276,33	-	22, 24, 25	-

* Average from 3 reverences

[1] Heiden A.C., Hoffmann A., Kolahgar, B., (2001), Comparison of the Sensitivity of Solid Phase MicroExtraction (SPME) and Stir Bar Sorptive Extraction (SBSE) for the Dertermination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Soil Samples, Gerstel AppNote 8/2001, http://www.gerstelus.com/appnotes/new/Gerstel%202001/an-2001-08.pdf
[2] NIST Chemistry WebBook, http://webbook.nist.gov/chemistry
[3] Tox Probe; Ten Carcinogens in Toronto; benzo[*a*]pyrene and other polycyclic aromatic hydrocarbons, http://www.city.toronto.on.ca/health/pdf/cr_appendix_b_pah.pdf
[4] Staffan Lundstedt; 2003, Analysis of PAHs and their transformation products in contaminated soil and remedial processes http://publications.uu.se/umu/fulltext/nbn_se_umu_diva-57.pdf

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5.4.2 Extraction

Water samples:

All vessels used for extraction were rinsed with deionised water, methanol and DCM before use. After thawing, 1 mL of 100 ng mL^{-1} internal standard solution was added to 0.5 L sample. After thorough mixing, the sample was filtered with a preextracted (10 mL DCM) glassfibre filter (GF/C, Whatman, Maidstone, England).

The filter was cut in small pieces and the particulate matter was extracted ultrasonically three times for 10 min with a mixture of dichloromethane/acetone (5:1 v:v). For the first step 15 mL and for the second and third step 10 mL of this mix were used. To remove particles the extract was cleaned with the SPE C18 cartridge used for the extraction of the dissolved PAHs. The extract was concentrated to about 0.5 mL by rotary evaporation (Büchi, Switzerland, 35°C, 700-500 hPa) and transferred to an amber glass GC-vial. The flask was then rinsed with DCM and the rinse was added to the extract. The whole volume was then concentrated to 1 mL (N_2) and the InjSTD was added.

The seawater filtrate was extracted by SPE using C18ec cartridges, which turned out to give the best recovery rate (see 4.2). Before extraction the cartridges were conditioned with 5 mL methanol, which was left for some time to soak into the SPE material. Then about 100 mL doubly de-ionised water followed by the sample were aspirated slowly over the cartridge using a vacuum pump (Saskia Hochvakuum). The sample flask was washed twice with 100 mL doubly de-ionised water which was aspirated over the cartridge as well, followed by 3 mL of a water/isopropanol (80:20) mixture.

For desorption of the PAHs 2 mL plus 3 mL DCM were used. From the resulting 5 mL extract 1 mL was transferred into an amber glass GC-vial and mixed with InjSTD TBrB .

All samples were measured randomLy within one gas chromatic run for each extraction. Concentrations and the proportions of the analyte between dissolved and particulate fractions were determined by using the ISTD closest to the retention time of the substance according to equations (8) to (11).

$$Conc_{vial} = \frac{\left(\frac{PA_{analyte}}{PA_{TBrB}} - CL_{section} \right)}{CL_{ascent}} \cdot Dil \qquad (8)$$

$Conc_{vial}$ = concentration of the analyte in the vial [ng mL^{-1}]
$PA_{analyte}$ = peak area determined by GC MS of the analyte
PA_{TBrB} = peak area determined by GC MS of TBrB
$CL_{section}$ = section of the calibration line
CL_{ascent} = ascent of the calibration line
Dil = dilution factor

$$R = \frac{PAH_{deut_solub} + PAH_{deut_part}}{PAH_{deut_add}} \cdot 100 \qquad (9)$$

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$$F_{solub} = \frac{PAH_{deut_solub}}{PAH_{deut_add}} \cdot 100 \quad F_{part} = \frac{PAH_{deut_part}}{PAH_{deut_add}} \cdot 100 \qquad (10)$$

R = recovery rate [%]
PAH_{deut_solub} = concentration of deuterated PAH determined for the soluble fraction [ng mL^{-1}]
PAH_{deut_part} = concentration of deuterated PAH determined for the particulate fraction [ng mL^{-1}]
PAH_{deut_added} = concentration of deuterated PAH added to the sample [ng mL^{-1}]
F_{solub} = soluble fraction of the deuterated PAH [%]
F_{part} = particulate fraction of the deuterated PAH [%]

$$Conc_{analyte} = \frac{\left(Conc_{vial_solub} + Conc_{vial_part}\right)}{R} \cdot F \cdot \frac{1}{V_{sample}} \cdot V_{Vial} \cdot 1000 \frac{ng}{\mu g} \qquad (11)$$

$Conc_{analyte}$ = concentration of the analyte in the water-sample [ng l^{-1}]
$Conc_{vial_solub}$ = concentration of the soluble fraction of the analyte in the vial [ng mL^{-1}]
$Conc_{vial_part}$ = concentration of the particulate fraction of the analyte in the vial [ng mL^{-1}]
F = soluble particulate fraction, respectively
V_{sample} = volume of the sample extracted
V_{Vial} = volume of the extract in the vial

Sediment and Mussel samples

Mussel samples were only taken once in Calais during the sampling in November. Those mussels were taken from a harbour stilt during ebb tide a point C0. About 60 mussels were collected randomly and put into a freeze bag. The extraction and analysis of these mussels was performed in the same way as described in section 6.3.2. To determine the accuracy of the extraction method a standard reference mussel tissue was extracted. This was obtained from LGC Promochem (NIST-2977 Mussel tissue - Organics and trace elements) and extracted twice at the same time as the mussels of the accumulation test.

Sediments were taken in July at points C1, C5, C700 and D5, in September at points C5, C700 and D700 and in November at points C5, C700 and D5. All samples were taken with a van Veen grab (Fig. 5), which takes abovut 150 cm² of the surface sediment, and were then transported to the lab in a freeze bag. There they were deep frozen at -18 °C until extraction. Before the extraction the sediment was freeze dried, coarse particles were removed and the remainder was ground in an agate ball mill for 30 min at 180 rpm. From this fine, dried sediment 5 g were weight into a glass bottle and the internal standard was added. The extraction was performed ultrasonically with 20 mL and two times 15 mL n-hexane for 15 min. As elemental sulphur negatively affects gas chromatographic analysis it was removed with elemental copper. Oxides on the copper surface were removed by washing three times with hydrochloric acid. The acid was removed by washing three times with deionised water and the water was removed by washing three times with methanol. The methanol and eventually remaining organic compounds bound to the copper surface were removed by washing three times with DCM. About ten of these cleaned and activated copper filings were than added to the extracts and left there for at least two hours. In those cases where the copper spans turned totally black (copper sulphide) again about ten pieces were added and left in the extract for additional two hours. The desulphurised extract was then filtered over $NaSO_4$ to remove the copper spans and remaining water

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from the extract and was then reduced to about 2 mL in a rotary evaporator. The clean-up was performed on a silica column (5 g silica deactivated with 5 % H_2O) and PAHs were eluted with 15 mL n-hexane and with 20 mL of a n-hexane and DCM (5:1) mix. Both extracts were combined, reduced to approximately 1 mL, transferred quantitatively into an amber glass 2 mL GC-vial and reduced to 1 mL under N_2. The injection standard was added and PAH concentrations were determined by GC-MS

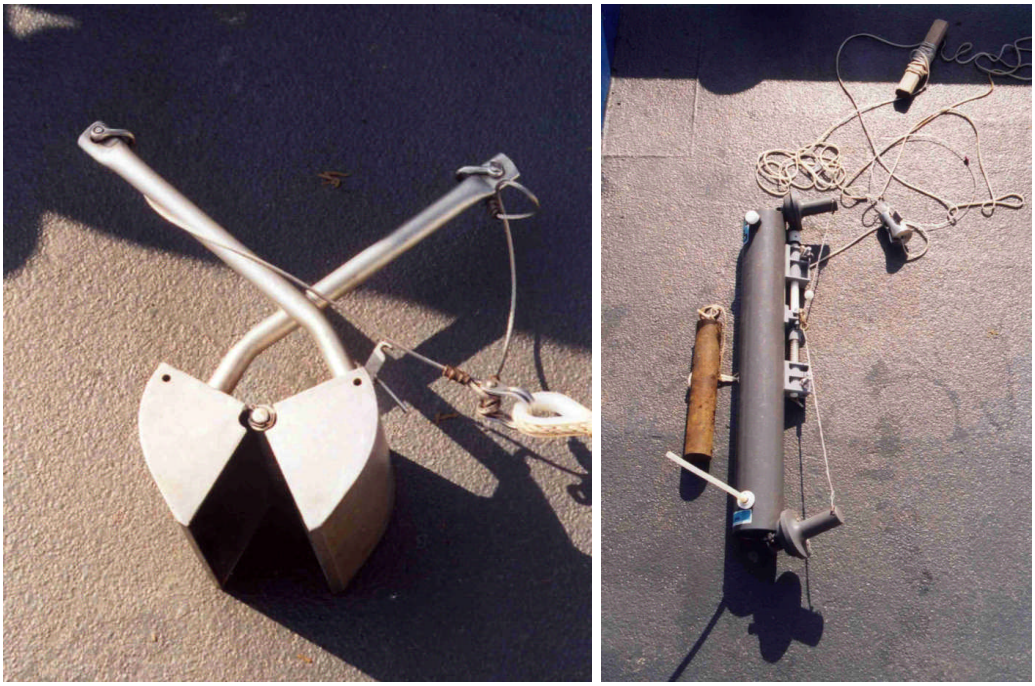

Fig. 5: Van Veen grab and Niskin sampler for sediment and water samples respectively.

5.4.3 Determination of the origin of PAHs

PAHs in the environment might have different origins. Although there are some natural sources such as oil seeps or some specific organisms, the main sources are anthropogenic. These include oil released during normal ship operation or from accidents and products of incomplete combustion of recent or fossil organic matter. To distinguish between these origins of a PAH mixture, some indices have been developed in the past. The major aspect used is the thermodynamic stability. For example phenanthrene (Phe) is thermodynamically more stable than its structural isomer anthracene (Anth). The same is valid for fluoranthene (Flu) and pyrene (Pyr) pair. Concerning to these facts the Phe/Anth ratio is higher in petrogenic (>10) than in pyrolytic pollution (<10). For Flu/Pyr a quotient of one was determined. Thus a Flu/Pyr ration>1 points to a pyrolytic, while a Flu/Pyr rations <1 indicates a petrogenic origin.

The chrysene (Chry) and benzo[*a*]anthracene (BaA) ratio is the basic for another index used. Chry and BaA are derived from combustion processes at high temperatures with a Chry/BaA ratio <1. Also an indicator for combustion derived PAHs is a higher abundance of four-, five- and six-ring PAHs in comparison to the two- and three-ring PAHs, prominent in petrogenic sources.

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An additional method which was used to determine the origin of the PAHs was principal component analysis and the regression of samples and compounds resulting in different regression charts. Principal component analyses (PCA) is a useful technique that has found application in fields such as face recognition and image compression, and is a common technique for finding patterns in data of high dimension. Therefore PCA has also been used to determine the origin of PAHs [Boehm et al., 1997; Stella et al., 2002; Burns et al., 1997; Branislav et al., 2001]. The background of this method is based in matrix algebra. In this case the analyses were performed by using a Matlab script, written by M. Hufnagl (see Appendix). In the first step the data are standardised by substracting the mean. The next step calculates the covariance matrix and then the eigenvector and the eigenvalues of this matrix. In this case the feature vector, which is later used for the transformation of the data, was only made up from the first two eigenvectors.

The regression of the compounds and the regression of the sampling points were performed using the statistic program Systat. The source code is similar to that one shown in the Appendix. In the literature this method was also used to determine PAH pollution sources [Adami et al. 2000].

5.5 Plankton samples

During the sampling in February and March plankton samples were taken in 50 mL bottles and analysed qualitatively. During the samplings in July, September and November plankton samples were taken from one, two and three meters water depth. From each depth one litre was taken with a Niskin sampler (Fig. 5) and all three water samples were collected in a three litre PVC bottle. In the laboratory the water was filtered over a 10 µm plankton net and 5 mL of the concentrated sample were transferred to an Uttermöhl counting chamber where the cells were allowed to settle overnight. The counting was performed with an inverted microscope. At 30 to 50 randomLy chosen points all plankton cells within the given grid of the microscope were counted. The concentration of the counted cells were then determined using the following equation

$$cells/ml = \frac{A \cdot 506.71}{fields \cdot 0.105626 \cdot V_{ex}} \cdot \frac{V_S}{V_{conc}}$$

where A is the amount of cells counted in the examined volume V_{ex}. V_S is the volume of the sample and V_{conc} is the volume of the concentrated sample.

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6 Material and Methods: Toxicity and accumulation tests

For these tests water was taken from the seawater scrubber inlet and outlet at point SCH1 and SCH2 during the fourth sampling which was performed in September. The samples were filled into Winkler-bottles (250 mL) which disabled the gas exchange between the samples and the atmosphere. This allows the examination of the samples in the laboratory at nearly unchanged conditions. The water samples, five from the inlet and five form the outlet, where transported to the lab in cooling boxes and then stored at 4 °C for two days before the toxicity tests were performed.

6.1 Lumistox

The bacterium used for this test was *Vibrio fischeri*. The enzymatically induced luminescence of this bacterium is quantitatively easy to determine. The reaction that takes place is that the enzyme luciferase oxidises chemical compounds like long chain aldehydes by aid of reduced FMN (flavin mononucleotide) and O_2 to the corresponding fatty acid. Within this reaction electrons are directly transferred from the $FMNH_2$ to the oxygen and energy is set free by emittance of light.

The test, produced by Dr. Bruno Lange GmbH, Berlin, is a standardized DIN (Deutsche Industrie Norm) method used to analyze the contamination of water. The test was performed according to the instructions given in the norm. From three different samples two parallels were screened resulting in six values for the inlet and six values for the outlet. As blank a 2 % NaCl solution was analyzed.

6.2 Brine shrimp test

Another possibility to determine the toxicity of a substance is the mortality of organisms exposed to that substance. Therefore during this test the mortality of juvenile and adult brine shrimp *Artemia salina* (Fig. 6) was observed after placing it into subsamples of the inlet and outlet water.

Fig. 6: Picture of *Artemia salina.* This organism was used for toxicity tests

Due to the natural habitat of *Artemia salina* this organism is able to build long lasting eggs. Two days before starting the test, about 200 mg of these eggs were placed into 1000 mL artificial seawater

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[RiPSUa et al., 1979]. For aeration an aquarium pump was used. From the seawater that included the hatched juveniles 1 mL with about 30 to 70 organisms were taken and pipetted into Petri dishes containing the inlet and outlet water (4 mL). The amount of individuals added was counted and after 6 h and 24 h the mortality was determined. The same was performed with 4 week old adult *Artemia salina* specimen. These were kept in an aquarium filled with seawater taken from the Jade Bay (Wilhelmshaven Germany) and fed with an *Isochrysis galbana* culture until the performance of the test. To prevent the organisms from starvation additionally 1 mL of this *Isochrysis galbana* culture was added.

6.3 Accumulation test

6.3.1 Preparation and Performance

This accumulation test was performed to assess the uptake of the released PAHs by mussels. Additionally it was used as toxicity test by observing the mussel mortality when exposed to the PAH concentrations observed in the outlet of the seawater scrubber. As a high volume of water was necessary for this test (2 m³) the water could not be taken directly from the inlet and outlet of the "Pride of Kent" and be transported to the laboratory in Germany. Therefore the PAH concentrations observed in the outlet samples of the seawater scrubber were determined and seawater taken from the Jade Bay in Wilhelmshaven Germany was spiked with the the major five observed PAHs.

Table 12: Categorisation of the accumulation tests.

number	assay	volume [l]	amount of mussels
1	particulate	17	30
2	control	17	30
3	dissolved	17	30
4	particulate	17	30
5	control	17	30
6	dissolved	17	30
7	particulate	17	30
8	control	17	30
9	dissolved	17	30
10	control external basin	12000	appr. 100

The test was separated into three subtests with three separate approaches (Table 12), three controls, three accumulation tests for PAHs bound to particulate material and three assays for the determination of accumulation of dissolved PAHs. For all experiments seawater taken from the Jade Bay was pumped into 1 m³ storage tanks and was centrifuged with a continuous centrifuge (Carl Padberg, Zentrifugenbau GmbH, Lahr Germany). The particulates were collected and freeze dried. The water was kept in another firmly closed 1 m³ storage tank from which 20 L canisters, one for every assay, were filled with 17 L of the seawater. These canisters were then placed into the laboratory where the assays were performed for temperature equilibration.

About 400 mussels (*Mytilus edulis*) were collected on a mussel bank (Swinnplate) from the backbarrier area of the East Frisian island Spiekeroog and placed into an external basin filled with approximately

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12 m³ seawater taken from the Jade Bay. From these mussels 270 species were chosen randomly and cleaned from barnacles, shell fragments and byssal threats. The cleaned mussels were laid into the aquariums each filled with 17 L of the water taken from the canisters. To prevent the mussels from lying directly on the ground of the aquarium and filtering their own faeces, plastic mats were placed on the bottom (Fig. 7). Aeration for all aquariums was by an aquarium pump (ACO-003, magnetic piston, 35 W, 3600 l/h), PVC tubes and aeration stones (Fig. 7).

Fig. 7: Photographs of the experimental design of the accumulation test. L.: all nine aquariums with aeration pump. M.: close view on to an aquarium with aeration stone and mussels placed on the PVC net. R.: mussels on PVC net.

Before starting the experiments the mussels were kept for 5 days in the aquarium to allow accommodation. Due to the low water volume in relation to the high amount of mussels, the water was exchanged twice during that time and later twice a week. Every day 2 mL of a highly concentrated *Phaeodactylum tricornutum* cultur were added to each aquarium. These algae were cultured in a 40 L bioreactor. Every second day 20 L were filtered over a plankton net (mesh size 10 µm). The concentrated *Phaeodactylum tricornutum* suspension was then stored at -18 °C.

Table 13: Mean PAH composition of the seawater scrubber outlet samples (March and July), PAH concentrations in the acetone solution and resulting PAH concentration in the aquaria

compound	mean % in samples	mg in 100 mL acetone	ng L^{-1} in aquarium
phenanthrene	100	5.125	1507
pyrene	42	2.142	630
chrysene	39	1.997	587
fluoranthene	17	0.872	256
anthracene	3	0.150	44

As explained above each subtest was performed with three separate approaches. For the assay with the particulate matter to each aquarium 2 mL algal suspension, 5 mL of a seston solution and 0.5 mL of a PAH solution in acetone was added. The seston solution contained the dried seston gained from the seawater used and additionally dried silt and clay to give an overall concentration of 240 mg L^{-1}. The addition of 5 mL of this solution to the water in the aquarium lead to a particle concentration of 70 µg L^{-1}. The composition of the PAH solution and the resulting PAH concentrations in the aquarium are given in Table 13. The phenanthrene concentration (1500 ng L^{-1}) was chosen because this was the maximum phenanthrene concentration detected in the outlet samples in March and July.

To the aquariua that contained the mussels for the dissolved test, also 0.5 mL of the acetone/PAH solution was added but instead of the seston, an aqueous quartz (Sigma Aldrich Laborchemikalien GmbH, Seelze, Germany) solution was added resulting in 70 µg L^{-1} quartz inside the aquarium. Quartz

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was chosen because it has only a small active surface and therefore only a low percentage of the PAHs adsorb to it. Therefore the PAHs, as intended, remain dissolved. Particulate material has to be added because otherwise the mussels would not be active and remain closed all the time. Before adding the quartz to the solution, it was ground in a wolfram crucible so that particle size decreased and the quartz particles lasted for a long time suspended in the water. To the controls both quartz and seston were added so that the water in the aquarium contained 70 µg L^{-1} of each.

The PAHs and the seston or quartz were added every day. Additionally 2 mL of the *Phaeodactylum* suspension were added. Water exchange was performed every third or fourth day (Table 14).

Table 14: Dates for water exchange during the accumulation test

	date	days
start	15.11.2004	0
1. water exchange	18.11.2004	3
2. water exchange	22.11.2004	7
3. water exchange	25.11.2004	10
4. water exchange	29.11.2004	14
5. water exchange	02.12.2004	17
6. water exchange	06.12.2004	21
7. water exchange	09.12.2004	24
8. water exchange	13.12.2004	28
9. water exchange	15.12.2004	30

6.3.2 Analysis and extraction of the mussels

After 30 days the tests the mussels of each aquarium were trasnferred to freezer bags and deep frozen at -18 °C. For each specimen shell length, total weight, shell weight as well as wet and dry weights (freeze drying) were determined. The mussels were than divided into size groups. As only few small mussels were available, mussels smaller than 50 mm were regarded as one class and mussels between 50 and 60 mm as another class. From both classes 7 specimen each were taken and ground in a wolfram crucible in a ball mill (Fritsch Pulverisette 5) over 30 min with a rotation speed of 120 rpm.

From the pulverized mussel tissue about 0.5 g were weighed into a glass flask and 5 mL of a 5M KOH solution and 1 mL of the internal standard (acenaphthene-D10, phenathrene-D10, chrysene-D12, perylene-D12) were added. The mixture was well mixed and left overnight to hydrolyse the cell walls. The following day the lysate was neutralized with 5 mL 5M hydrochloric acid. Then 5 mL deionised water and 40 mL n-hexane (Pestanal, Sigma Aldrich, Seelze, Germany) were added. This viscous solution was placed into an ultrasonic bath for 15 min to separate the organic and aqueous phases. The organic phase was transferred into a roundbottom flask and the procedure was repeated twice with 30 mL n-hexane. The combined extracts were filtered over $NaSO_4$ to remove remaining water and then evaporated to a final volume of about 2 mL. After quantitative transfer to a silica column (10 g, 5 % deactivated with H_2O) PAHs were eluted with 35 mL n-hexane and 40 mL of a n-hexane/DCM solution (5:1 v:v). Both fractions were combined and the solvents evaporated to about 1 mL which was transferred quantitatively into a 2 mL amber glass GC vial. After n-hexane evaporation to 1 mL under N_2 the injection standard was added.

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To check the constitution of the mussels, the fat content was determined according to Smedes and also the condition index (CI) was determined as the quotient of dry weight and shell weight multiplied with 100. This index can be interpreted as an index of growth [Smaal and Staben 1990] and as an indirect reflection of the food availability [Pérez Camacho et al 1995]. The fat content was determined for one mussel of each assay and the CI was determined for all mussels and the mean was calculated for each run.

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7 Results

7.1 pH-Mixtures

7.1.1 Jade Bay, Wilhelmshaven, Germany

In Fig. 8 and Fig. 9 the time-dependent results for the mixtures of natural acidified Jade Bay seawater are shown. Fig. 9 also shows the pH in equilibrium in dependency of the percentage of pH 4 seawater in the mixture. The mixtures stirred with 250 rpm with a total volume of 500 mL reach equilibrium after about 24 hours. The higher the stirring speed the faster the equilibrium is reached. For the 50 % mixture stirred with 1000 rpm equilibrium is reached after about 2 hours, while the unstirred sample needed over 72 h. A similar behaviour can be observed for the 50 % mixtures with different volumes (100 mL, 250 mL, 500 mL, 1000 mL) but the same stirring speed (250 rpm). The greater the volume the longer the time until the equilibrium is reached. The 100 mL:100 mL mixture needed about 8 h whereas the 1000 mL:1000 mL mixture again needed over 72 h.

The results for all 500 mL mixtures (250 rpm) in equilibrium show that there is no significant change up until 50 % acidified water were added and a change is mainly evident between 80 %, 90 % and 100 % (Fig. 2 left).

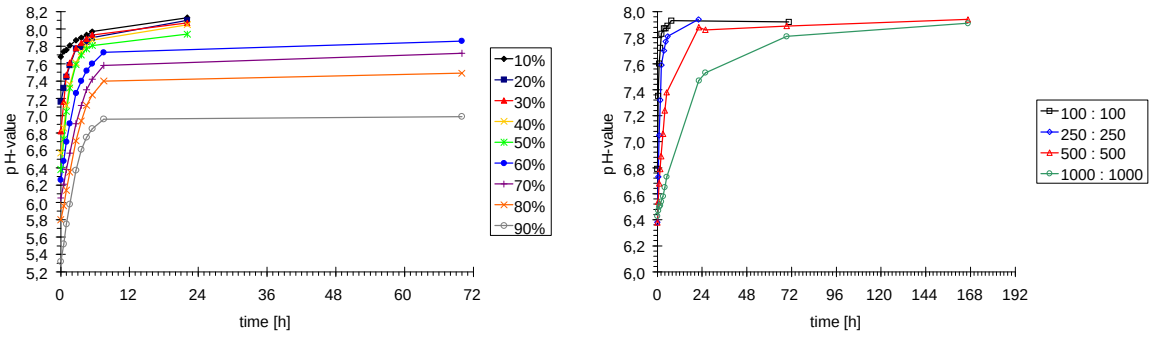

Fig. 8: Left: Different amounts of acidified (pH 4) Jade Bay seawater mixed with non-acidified Jade Bay seawater. Given is the development of pH over time in relation to the percentage of pH 4 water. Right: same as left but only 50:50 mixing ratio with different volumes.

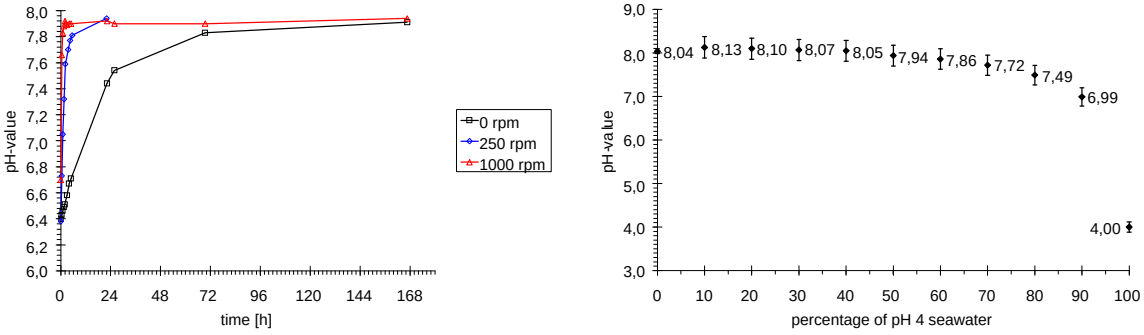

Fig. 9: Left: 50:50 mixing ratio of acidified (pH 4) Jade Bay and natural Jade Bay seawater, with different stir bar rotation speeds. Right: pH-value in equilibrium as function of mixing ratio (% pH 4 seawater)

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7.1.2 Ems River, Papenburg, Germany

Fig. 10. shows the results for the pH mix test determined with Ems River water taken at the Meyer Werft in Papenburg, Germany. Although the water had only a very low salinity it shows a similar behaviour to the experiment performed with seawater. This is due to its high sediment load and therefore high carbonate content. The equilibrium in this case is reached as fast as in the test with Jade Bay seawater, after about 12 h. However, a continuous decrease in pH can be observed in 1:1 mixtures (100 mL) until the percentage of pH 4-water has reached about 80 %.

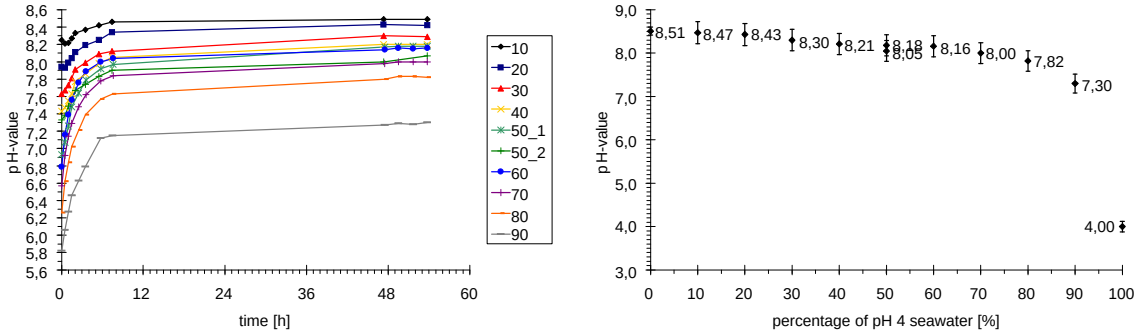

Fig. 10: Left: Different amounts of acidified (pH 4) Ems River water mixed with non-acidified Ems River water. Given is the development of pH over time. Right: pH-value in equilibrium as function of mixing ratio (% pH 4 seawater)

7.1.3 Odense, Denmark

Fig. 11 shows the results for the tests performed with Odense seawater. Also in this case equilibrium is reached within about 12 h after mixing the two water bodies. The first significant change is observable for mixtures containing more than 50 %.pH 4-water.

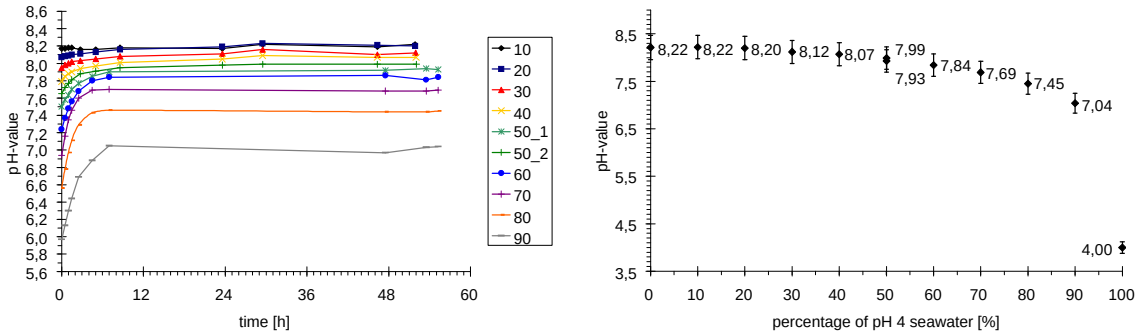

Fig. 11: Left: Different amounts of acidified (pH 4) Odense seawater mixed with non acidified Odense seawater. Given is the development of pH over time. Right: pH-value in equilibrium as function of mixing ratio (% pH 4 seawater)

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7.1.4 Calais, France

Fig. 12 shows the results obtained with Calais seawater. Noticeable in this case is that there is, for all mixtures up to 60 % pH 4-seawater, no temporal behaviour of the pH until the equilibrium is reached. For the rest of the mixtures equilibrium is reached after maximally 6 h. A change of the pH in equilibrium out of the error range is first observable at a percentage of 60 % pH 4-seawater.

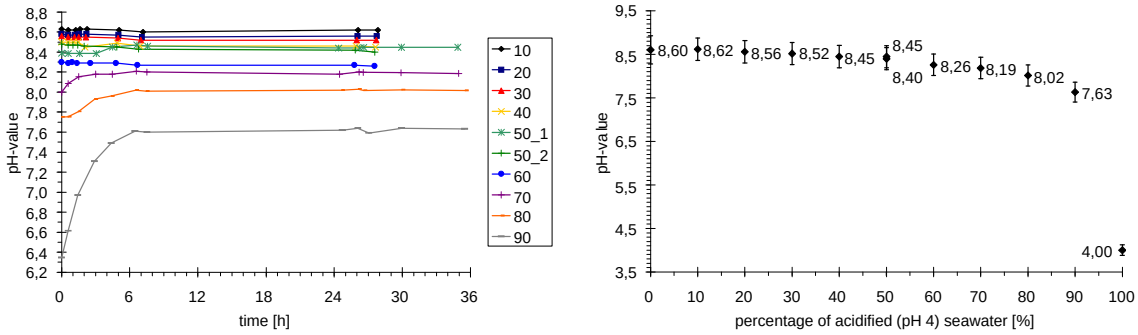

Fig. 12: Left: Different amounts of acidified (pH 4) Calais seawater mixed with non acidified Calais seawater. Given is the development of pH over time. Right: pH-value in equilibrium as function of mixing ratio (% pH 4 seawater)

7.1.5 Dover, England

A similar behaviour as observed for Calais seawater was found for Dover seawater. Fig. 13 shows the results for this test. For a mixing ration of 50:50 no significant temporal development of the pH can be observed. The first pH change in equilibrium greater than the error range is observable for percentages greater than 50 % pH 4-seawater

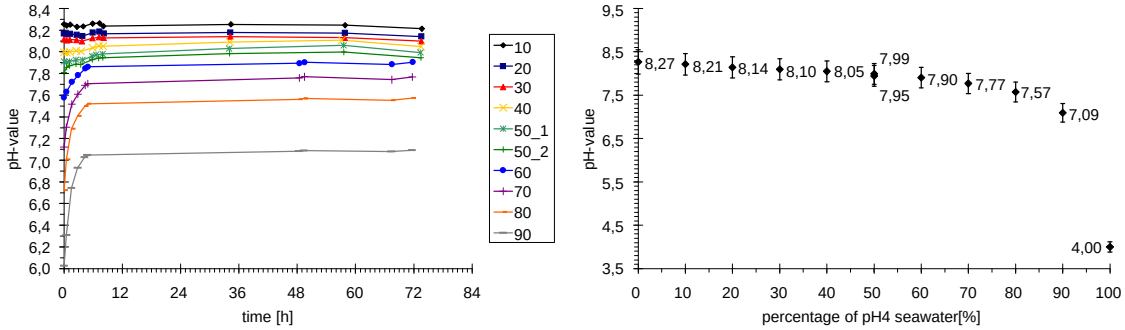

Fig. 13: Left: Different amounts of acidified (pH 4) Dover seawater mixed with non acidified Dover seawater. Given is the development of pH. Right: pH-value in equilibrium as function of mixing ratio (% pH 4 seawater)

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7.1.6 Comparison of all results (in equilibrium)

Looking at the figures Fig. 8 to Fig. 13 it can be seen that during the experiments with Ems river water, Nassau harbour and Odense seawater the mixtures are in equilibrium after about the same time. For Dover and Calais seawater, equilibrium is reached much faster.

In equilibrium all values, even the river water values, are about the same. Highest values were observed for Calais seawater. Dover Jade and Odense values in equilibrium are, when error range of the pH meter is taken in consideration, the same for all mixtures.

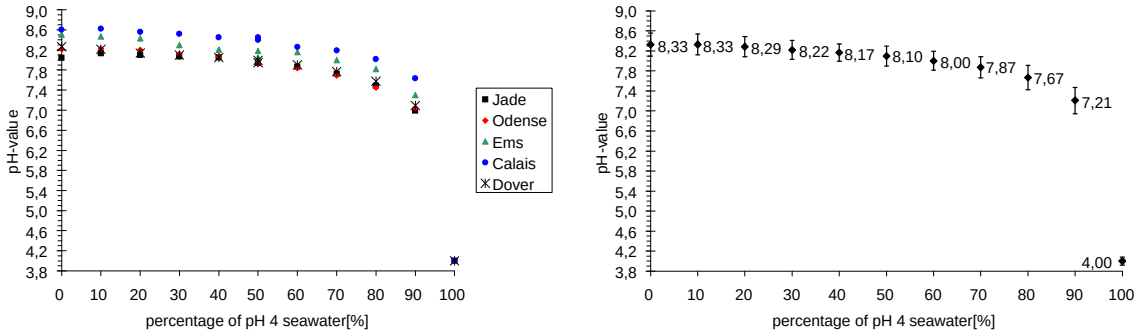

Fig. 14: Left: pH-value in equilibrium of mixing ratio (% pH 4 seawater) for all pH tests. Right: Mean of all tests with standard deviation.

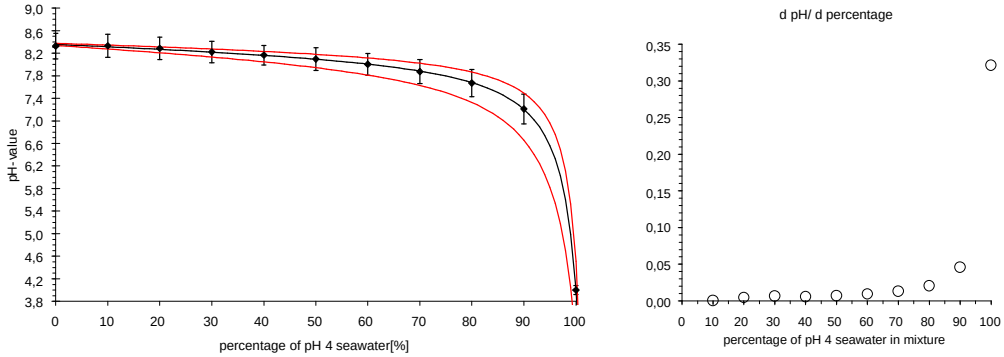

Fig. 15: Left: mean pH value (points) and standard deviation (error bars) in equilibrium of mixing ratio (% pH 4 seawater) for all pH tests. The black line shows the model fitted to the points and the red line shows the 95 % confidence interval of the model. Right: change of pH over percentage

From all pH values determined for the different mixtures in equilibrium the mean and the standard deviation was calculated and plotted against the percentage of the pH 4 water in the mixture. For these values an easy function was searched which fits the values best. Therefore the free available software LAB fit (LAB fit Curve fitting software V 7.2.6.) was used. The determined function

$$pH - value = \frac{a + percentage}{b + c \cdot percentage} + d \cdot percentage \qquad (12)$$

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was then fitted to the data by using the software Systat 8.0 (command file see appendix). The result is shown in Fig. 15. The raw R-square (1-Residual/Total), the mean corrected R-square (1-Residual/Corrected) and the R (observed vs. predicted) square values, which were calculated with Systat, equalled 1.000.

The values obtained are listed in Table 15. For 0 % the pH is defined as $pH = \frac{a}{b}$.

Table 15: Values obtained by fitting equation 12 to the pH-values

parameter	low 95 %	optimum	up 95 %
A	-101.784	-101.646	-101.508
B	-12.209	-12.1645	-12.120
C	0.117	0.117793	0.118
D	-0.004	-0.00273782	-0.002

According to this function it is possible to mix natural seawater with acidified seawater in a relation of 60:40 to give a pH change of 0.2 pH units. According to the EPA regulations 0.2 units is maximum allowed pH change in the initial mixing zone.

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7.2 GC-MS Validation

For GC MS validation, one time three different dilution series with concentrations of 1, 10, 50 and 100 ng l^{-1} and one series made of 9 dilutions (2.5, 25, 25, 50, 50, 100, 250, 500, 1000 µg l^{-1}) in which some dilutions were prepared double but were diluted down from different concentrations. From this series one of the 25 µg l^{-1} and the 500 µg l^{-1} concentrations were measured 8 times.

The three different dilution series were prepared to estimate the error due to the handling and the diluting (Table 16). The calibration series with the nine different steps was prepared to determine the linearity of the GC MS and the 8-fold measurements were performed to determine the accuracy of the GC MS including the integration of the peak areas.

From Table 10 it can be seen that the relative standard error for the three different dilution series is low. As the stock solution is a mix of all PAHs, it is admissible to calculate the mean of all compounds. Therefore the error concerning to handling, loss to the walls of the vessels and additionally the GC MS is 5.4 %. The accuracy of the GC MS alone is listed in Table 17.

The accuracy for the low molecular weight PAHs is higher than for the high molecular PAHs. The difference between the relative standard deviations of low and high concentrations is to due to to mathematical reasons. If the peak area error is always the same, the relative error is higher for low peak areas than for higher peak areas. As all samples were concentrated within the range of 25 to 500 ng mL^{-1} it is admissible to calculate the mean of all standard deviations, which results in 2.5 %. This is about the half of the relative standard deviation calculated for the three different dilution series.

Table 16: Standard deviation of three different standard dilution series.

compound	rel. stand dev.
acenaphthylene	4.7
acenaphthene	4.7
acenaphthene-D10	9.7
fluorene	4.9
phenanthrene-D10	4.5
anthracene	6.0
phenanthrene	5.1
fluoranthene	4.1
pyrene	5.8
benz[*a*]anthracene	6.4
chrysene-D12	6.8
chrysene	9.7
benzo[*b*]+benzo[*k*]fluoranthene	5.4
benzo[*a*]pyrene	4.1
perylene-D12	3.6
dibenz[*a,h*]anthracene	2.4
benzo[*ghi*]perylene	3.7
indeno(1,2,3,*c,d*)pyrene	5.1
mean	5.4

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Table 17: Accuracy of the GC/MS analysis (including InjSTD, integration and measurement)

compound	mean 25 µg L^{-1}	std. dev. 25 µg L^{-1}	rel. std. dev. 25 µg L^{-1}	mean 500 µg L^{-1}	std. dev. 500µg l^{-1}	rel. std. dev. 500 µg L^{-1}
acenaphthylene	0.133	± 0.002	± 1.4	2.865	± 0.015	± 0.5
acenaphthene	0.086	± 0.001	± 1.4	1.848	± 0.009	± 0.5
acenaphthene-D10	0.066	± 0.001	± 0.8	1.407	± 0.006	± 0.4
fluorene	0.092	± 0.002	± 1.6	2.029	± 0.011	± 0.5
phenanthrene-D10	0.110	± 0.001	± 0.8	2.382	± 0.007	± 0.3
phenanthrene	0.142	± 0.002	± 1.2	3.117	± 0.019	± 0.6
anthracene	0.133	± 0.002	± 1.1	2.982	± 0.019	± 0.7
fluoranthene	0.134	± 0.002	± 1.2	2.978	± 0.016	± 0.5
pyrene	0.135	± 0.002	± 1.8	2.975	± 0.017	± 0.6
benz[*a*]anthracene	0.090	± 0.005	± 5.5	2.449	± 0.069	± 2.8
chrysene-D12	0.083	± 0.003	± 3.1	2.281	± 0.018	± 0.8
chrysene	0.103	± 0.004	± 3.8	2.707	± 0.032	± 1.2
benzo[*b*]fluoranthene +benzo[*k*]fluoranthene	0.168	± 0.009	± 5.4	4.608	± 0.072	± 1.6
benzo[*a*]pyrene	0.056	± 0.004	± 7.2	1.609	± 0.045	± 2.8
perylene-D12	0.045	± 0.003	± 6.5	1.263	± 0.031	± 2.4
dibenz[*a,h*]anthracene	0.028	± 0.003	± 9.4	0.868	± 0.033	± 3.8
benzo[*ghi*]perylene	0.040	± 0.002	± 5.9	1.065	± 0.024	± 2.3
indeno(1.2.3.*c.d*)pyrene	0.030	± 0.002	± 7.5	1.015	± 0.031	± 3.0

Table 18: F-Test for linearity of the GC/MS analysis. Shown results were calculated for all dilution steps ranging from 2.5 to 1000 µg L^{-1}

compound	$s^2_{y_linear}$	$s^2_{y_nonlinear}$	DS²	EV	F (1.6)	
acenaphthylene	33.39	13.75	151.27	11.00	13.745	linear
acenaphthene	33.39	13.75	151.27	11.00	13.745	linear
acenaphthene-D10	20.01	6.03	103.93	17.24	13.745	linear
fluorene	30.66	33.53	13.40	0.40	13.745	linear
phenanthrene-D10	21.90	15.16	62.34	4.11	13.745	linear
phenanthrene	33.10	35.98	15.79	0.44	13.745	linear
anthracene	114.90	101.42	195.76	1.93	13.745	linear
fluoranthene	111.32	85.86	264.07	3.08	13.745	linear
pyrene	110.49	70.20	352.21	5.02	13.745	linear
benz[*a*]anthracene	1999.05	316.49	12094.41	38.21	13.745	nonlinear
chrysene-D12	686.38	265.45	3211.96	12.10	13.745	linear
chrysene	342.60	241.16	951.23	3.94	13.745	linear
benzo[*b*]fluoranthene	2050.00	419.41	11833.50	28.21	13.745	nonlinear
benzo[*k*]fluoranthene benzo[*a*]pyrene	2410.91	222.39	15542.04	69.89	13.745	nonlinear
perylene-D12	2583.90	277.91	16419.87	59.08	13.745	nonlinear
dibenz[*a.h*]anthracene	1834.48	125.87	12086.15	96.02	13.745	nonlinear
benzo[*ghi*]perylene	1558.59	190.58	9766.67	51.25	13.745	nonlinear
indeno(1.2.3.*c.d)*pyrene	2554.00	343.29	15818.21	46.08	13.745	nonlinear

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The results for the check on linearity are shown in Table 18 and Table 19. For the low molecular weight PAHs linearity is given for a range from 2.5 to 1000 ng mL^{-1}. This group includes acenaphthylene, acenaphthene, acenaphthene-D10, fluorene, phenanthrene-D10, phenanthrene, anthracene fluoranthene, pyrene, chrysene and chrysene-D12. For the high molecular weight PAHs a lower linear range was determined. This group includes benz[*a*]anthracene, benzo[*b*]fluoranthene + benzo[*k*]fluoranthene, benzo[*a*]pyrene, perylene-D12, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene and indeno(1,2,3,*c,d*)pyrene. The linearity for these PAHs ranged from 1 to 100 ng mL^{-1}.

Based on these results all samples with a concentration above the determined linearity range were diluted to a concentration within this range.

Table 19: F-Test for linearity of the GC/MS analysis. Results were calculated with all dilution steps ranging from 2.5 to 100 µg L-1

compound	$s^2_{y_linear}$	$s^2_{y_nonlinear}$	DS²	EV	F (1,6)	
benz[*a*]anthracene	4.21	1.245424	13.1	10.52	21.198	linear
benzo[*b*]fluoranthene	9.766	3.208492	29.44	9.175	21.198	linear
benzo[*k*]fluoranthene						
benzo[*a*]pyrene	4.932	2.068914	13.52	6.534	21.198	linear
perylene-D12	5.842	455.1465	-1342	2.949	21.198	linear
dibenz[*a,h*]anthracene	11.4	5.994801	27.6	4.605	21.198	linear
benzo[*ghi*]perylene	7.665	6.968051	9.756	1.4	21.198	linear
indeno(1,2,3,*c,d)*pyrene	7.988	8.354367	6.889	0.825	21.198	linear

The limit of detection was determined as three times the 25 ng mL^{-1} concentration standard deviation. The results are shown in Table 20.

Table 20: Limit of detection (LOD) for determined PAHs

compound	LOD [ng mL^{-1}]
acenaphthylene	1
acenaphthene	1
acenaphthene-D10	1
fluorene	2
phenanthrene-D10	1
phenanthrene	1
anthracene	1
fluoranthene	1
pyrene	1
benz[*a*]anthracene	4
chrysene-D12	3
chrysene	3
benzo[*b*]fluoranthene	4
benzo[*k*]fluoranthene	
benzo[*a*]pyrene	5
perylene-D12	5
dibenz[*a,h*]anthracene	8
benzo[*ghi*]perylene	4
indeno(1,2,3,*c,d)*pyrene	5

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7.3 PAH-Extraction, Validation of Method

As in the most cases PAHs are extracted from fresh water or sediments most applications are fitted for these matrices. Therefore tests (Chapter 4.2) were performed to determine the extraction efficiency, the accuracy and the reproducibility of the method.

As there is no reference material for PAH in seawater available, for the recovery tests a certified PAH mix in acetone was diluted, added to seawater and extracted as described before. The results of the tests with the different SPE sorbents and the different elution solvents (Table 21) show that the best recovery rate with the lowest standard deviation was obtained with the SPE C18ec cartridges and DCM as elution solvent. The EASY material showed only low recovery rates (Fig. 16) for the high molecular PAHs. The same was observed when using SPE C18ec and n-hexane (Fig. 17) as elution solvent. Almost as good results as for C18ec and DCM were observed for C18 PAH SPE sorbent (Fig. 18). But as these cartridges were only available with a load of 500 mg, the flow was much slower and the drying took longer than for C18ec. Therefore in all assays C18ec cartridges and DCM were used to extract the soluble fraction of the PAHs. LLE also showed good recovery rates, but PAHs with high vapour pressure were lost during evaporation in the rotary evaporator.

The recovery rate in natural seawater in Fig. 19 was low for high molecular PAHs when only the liquid fraction was considered. Therefore additionally the filter was extracted. The results are shown in Fig. 21. Highest recovery rates close to 100 % were observed for fluorene, phenanthrene, pyrene and dibenz[*a,h*]anthracene. The lowest recovery rate was determined for chysene-D12 with 66.4 %. The mean recovery rate for all compounds was determined to be 86.1 % ± 10.6.

Fig. 20 shows that >90 % of acenaphthylene, acenaphthene, fluorene, phenanthrene-D10 and anthracene are present in the dissolved form. Benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, perylene-D12, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene and indeno(1,2,3,*c,d*) pyrene are mainly (>90 %) adsorbed to particles. Benz[*a*]anthracene, chrysene and chrysene-D12 are distributed about 50:50 between particulate and aqueous phase. The results of this test showed that a the highest recoveries were found after 2 h and 4 h. Extraction time had a significant influence on phenanthrene, benz[*a*]anthracene, chrysene-D12 and chrysene only. For these compounds the soluble fraction was rising with time.

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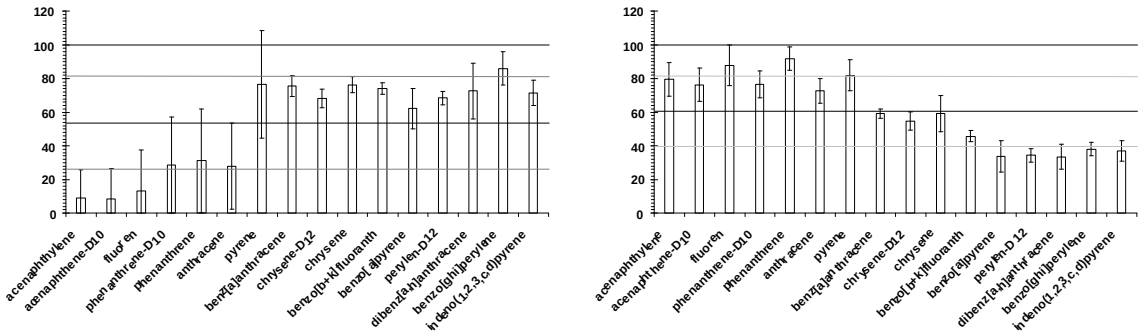

Fig. 16: Results of tests for the determination of the recovery rates of PAHs from seawater. Left: Results of Liquid-Liquid-Extraction. Shown are the recovery rates for the different PAHs and the overall mean and standard deviation. Right: Same for extraction with SPE sorbent Chromabond EASY.

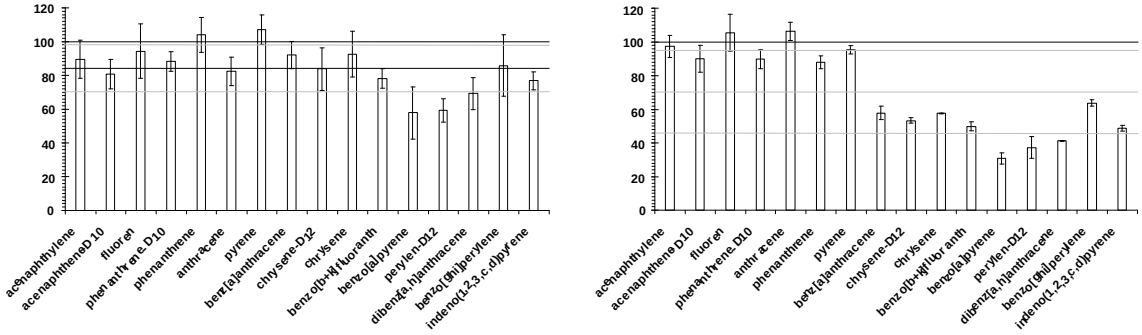

Fig. 17: Results of tests for the determination of recovery rates of PAHs from seawater. Left: Extraction by SPE with sorbent Chromabond C18 ec with elution solvent DCM. Shown are the recovery rates for the different PAHs and the overall mean and standard deviation. Right: Same for SPE sorbent Chromabond C18 ec but with elution solvent n-hexane.

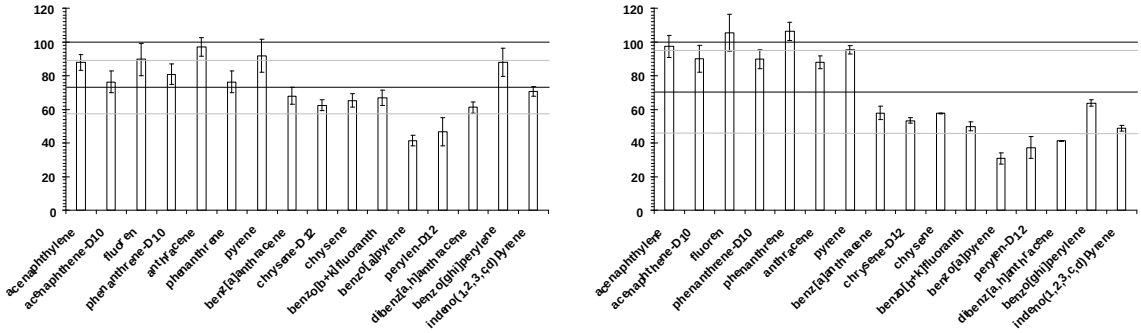

Fig. 18: Results of tests for the determination of recovery rates of PAHs from seawater. Left: Extraction by SPE with sorbent Chromabond C18 PAH with elution solvent DCM. Shown are the recovery rates for the different PAHs and the overall mean and standard deviation. Right: Influence of addition of different amounts of acetone to the sample.

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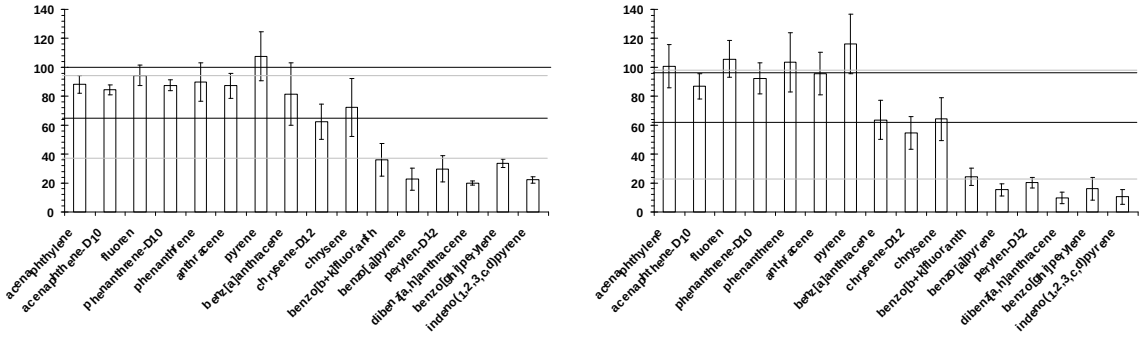

Fig. 19: Recovery rates of the soluble PAHs from natural seawater with Chromabond SPE sorbent C18 ec and elution solvent DCM. Left: Calais seawater Right: Dover seawater.

Table 21: Mean recovery rates and standard deviations determined for tests with artificial seawater.

PAH	EASY		C18PAH		C18ec/ DCM		C18ec/Hexane		LLE	
	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
acenaphthylene	79.6	10.0	87.9	4.7	89.5	11.3	97.4	6.5	9.0	16.9
acenaphthene-D10	76.3	9.8	76.3	6.4	80.8	8.5	90.1	8.0	8.3	18.3
fluorene	87.8	12.0	89.6	9.6	94.4	16.2	105.5	11.0	13.2	24.4
phenanthrene-D10	76.6	7.9	80.8	6.1	88.4	5.7	89.8	5.5	28.4	28.5
phenanthrene	91.9	6.9	97.0	5.6	104.0	10.6	106.4	5.4	31.2	30.8
anthracene	72.8	7.3	76.3	6.5	82.5	8.5	88.1	3.8	28.0	25.7
pyrene	81.9	9.1	91.9	9.7	107.3	8.7	95.3	2.3	76.6	32.0
benz[*a*]anthracene	59.0	2.8	67.9	5.1	92.2	8.1	57.9	4.1	75.5	6.3
chrysene-D12	54.8	5.3	62.4	3.4	83.9	12.7	53.3	1.5	68.3	5.6
chrysene	59.1	10.7	65.1	4.0	92.5	13.6	57.6	0.3	76.2	4.7
benzo[*b*]fluoranthene +benzo[*k*]fluoranthene	45.6	3.3	66.7	4.4	78.1	5.7	49.9	2.7	74.1	3.5
benzo[*a*]pyrene	33.7	9.4	41.4	3.3	57.8	15.5	30.8	3.2	62.1	11.9
perylene-D12	34.3	4.0	46.6	8.4	59.4	6.9	37.2	6.5	68.4	4.0
dibenz[*a,h*]anthracene	33.5	7.4	61.1	3.2	69.3	9.5	41.3	0.1	72.6	16.5
benzo[*ghi*]perylene	38.1	3.9	88.1	8.4	85.8	18.2	63.7	2.0	86.0	9.8
indeno(1,2,3,*c,d)*pyrene	36.9	6.0	70.5	2.7	76.9	5.4	48.7	1.6	71.4	7.4
mean + standard deviation	60.1	21.1	73.1	16.0	84.0	13.8	69.6	25.8	53.1	27.9

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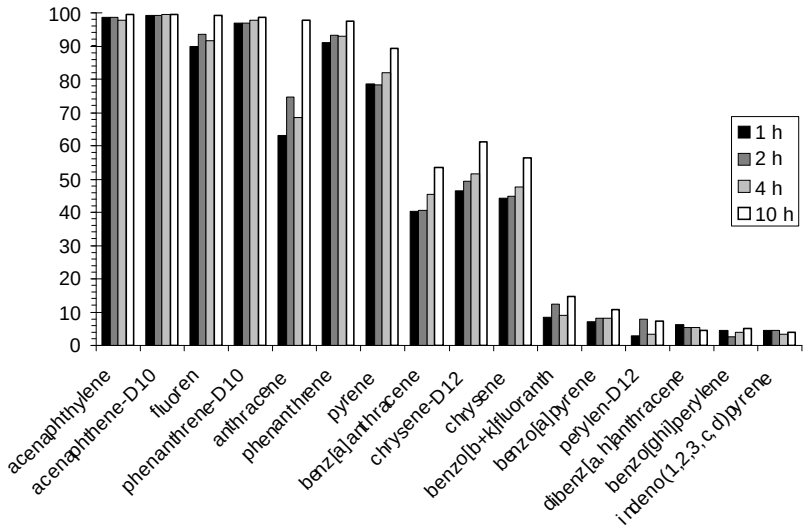

Fig. 20: Fractionation of PAHs between dissolved and particulate fraction after different incubation times.

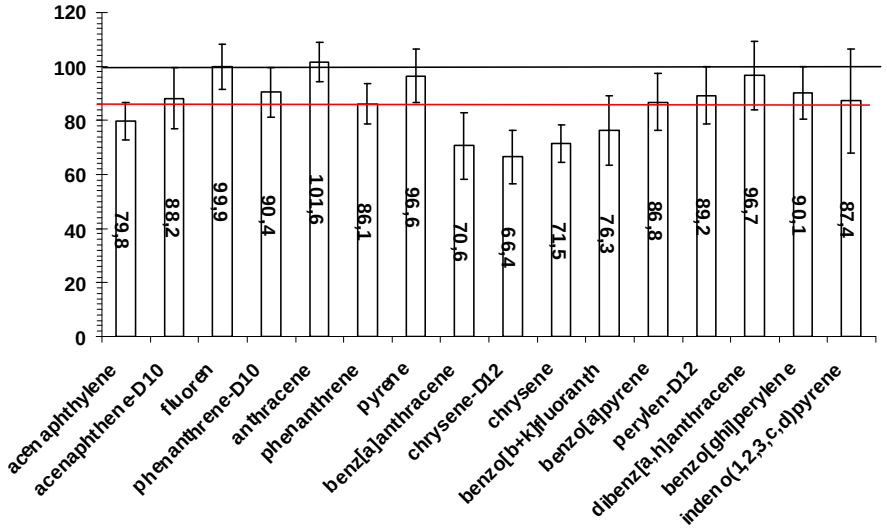

Fig. 21: Mean recovery rate and standard deviation for eight extractions of Dover seawater and particulate fraction.

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8 Results and Discussion of environmental samplings

In this chapter the results of the different samplings are shown. The pH, salinity, temperature, metal, sulphate, nutrients, plankton and PAH data will first be shown and described for each sampling and then the variations over the annual circle will be presented.

8.1 1st sampling (February)

8.1.1 pH, Temperature, Salinity, Conductivity, Oxygen

Table 22 shows the pH, water temperature, air temperature, salinity and oxygen contents measured during the sampling on 11.02.2004. The most eastern point (Point Cal 2: Quai de service) showed the lowest pH and the lowest salinity. The highest salinity (31 PSU) was observed for the point the closest to the open sea. The temperature was nearly the same for all points. Only at Cal 1 (Quai en eau profonde) water temperature was a little lower (8.2 °C). Oxygen was saturated at all points.

Table 22: Air and water temperature [°C], salinity [PSU], pH value and oxygen [mg l^{-1}] during sampling in Calais harbour on 11.2.2004

		temp. air [°C]	temp. water [°C]	salinity [PSU]	pH	oxygen [mg L^{-1}]
Cal 1	Quai en eau profonde	8.2	7.4	27.0	7.97	9.7
Cal 2	Quai de service	8.8	7.3	18.3	7.81	9.3
Cal 3	Quai de la Loire	8.8	7.3	29.6	8.04	10.3
Cal 4	Jetee ouest	8.8	7.4	31.0	8.02	8.4

All samples in Calais were taken between 8:45 am and 10:30 am (CET). According to Table 8 low tide was at 10:45 am, so all samples were taken during ebb tide. All samples in Dover were taken between 18:30 and 19:00 (CET). According to Table 8 low tide on 11.2.2004 was at 21:39. Therefore all samples in Dover were also taken at ebb tide.

Table 23 shows the water temperature, the salinity and the pH for the samples taken in Dover during the sampling on 11.02.2004. For all stations the results are similar. pH was with 8.10 higher than in Calais. The temperature 8.4 °C was about 0.4 °C colder and salinity was about 3 units higher than in Calais.

Table 23: Water temperature [°C], salinity [PSU] and pH-value during sampling in Dover harbour on 11.2.2004 and on board of the “Pride of Kent”

		temp. water [°C]	salinity [PSU]	pH
Point 7	Harbour entrance	8.5	34.1	8.10
Point 8	Middle port	8.4	34.0	8.10
Point 9	Quay 4	8.1	34.1	8.11
Point SCH1	Channel SWS inlet	9.2	34.3	8.06
Point SCH2	Channel SWS outlet	22.3	34.9	7.99

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Despite dilution by the cooling water the temperature was higher in the outflow than in the inlet water (inlet 9.2 °C outlet 22.3°C). Although this increase will have no or only little direct influence on the ecosystem it will influence the physical behaviour of the effluent. Higher temperatures at constant salinity increase the buoyancy of the effluent in comparison to the surrounding water. This may partially hinder the water bodies from effective mixing. A change in salinity, which would support or reduce this effect, was not observed. Another effect of higher water temperatures is the lower solubility of gaseous compounds in warmer water. This could lead to oxygen depletion. As oxygen was saturated in all samples no adverse effect was observed. Besides, a negative effect of cooling water discharges from ships on the surrounding environment was, concerning to the knowledge of the author, never reported.

8.1.2 Metals and Sulphate

Metal and sulphate concentrations determined by ICP-OES are shown in Table 25. The determined metals are listed in chapter 5.3 on page 15. Concentrations below the detection limit are marked by a dash. The concentration of the sea salt standard (International Association for Physical Science of the Ocean, IAPSO) are given in Table 24.

Table 24: Contents of the International Association for Physical Science of the Ocean standard for natural Atlantic seawater.

element	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg
unit	ppb	ppm	ppb	ppb	ppb	ppb	ppb	ppm	ppb	ppm
concentration	14	412	0.01	0.05	0.04	0.1	2	387	180	1294

element	Mn	Mo	Ni	Pb	SO4	Sr	V	Zn
unit	ppb	ppb	ppb	ppb	ppm	ppb	ppb	ppb
concentration	0.2	10	0.2	0.003	2712	8000	2.5	0.1

During the sampling on 11.2.2003 none of the examined transition metals were found inside the harbours with the exception of Calais point Cal 2: Quai de service. Here a manganese concentration of 69 ppb was detected. At this point earth metals were with the exception of barium lower in comparison to the other points, whereas at the harbour entrance in Dover Ba, Li, Sr, Ca, K and Mg concentrations were slightly higher than at the other points. The sulphate concentration was highest at this point too. Both, the high sulphate and the high earth metal concentrations are mainly due to the higher salinity at this point. The comparison between seawater scrubber inlet and outlet water showed a slight increase of the zinc concentration in the outlet water. This is most probably due to a contamination from for example the tubing, the fittings or the pumps.

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Table 25: Sulphate, earth and transition metals determined for the samples taken on 11.02.2004. Fields with"-" show concentrations below the detection limit.

		Cal 1	Cal 2	Cal 3	Cal 4	7	8	9	21	22
Ba	ppb	17	21	18	16	20	14	14	13	12
Ca	ppm	339	263	359	369	509	391	390	395	401
Cd	ppb	-	-	-	-	-	-	-	-	-
Co	ppb	-	-	-	-	-	-	-	-	-
Cr	ppb		-	-	-	-	-	-	-	-
Cu	ppb	-	-	-	-	-	-	-	-	-
Fe	ppb	-	-	-	-	-	-	-	-	-
K	ppm	280	180	310	352	475	352	373	357	376
Li	ppb	148	112	161	169	232	185	186	181	185
Mg	ppm	994	664	1071	1113	1567	1183	1191	1219	1254
Mn	ppb	-	68	-	-	-	-	-	-	-
Mo	ppb	-	-	-	-	-	-	-	-	-
Ni	ppb	-	-	-	-	-	-	-	-	-
Pb	ppb	-	-	-	-	-	-	-	-	-
SO4	ppm	2161	1479	2399	2461	3831	2857	2853	2842	2874
Sr	ppb	6392	4448	6853	7223	10188	7889	7863	7907	8093
V	ppb	-	-	-	-	-	-	-	-	-
Zn	ppb	-	-	-	-	-	-	-	-	143

8.1.3 Nutrients

Table 26 shows the nutrients concentrations determined for the samples taken on 11.02.2004. The following abbreviations are used. Total chlorophyll (THCL), particulate inorganic phosphorus (PIP), particulate organic phosphorus (POP), total particulate phosphorus (TPP), reactive dissolved phosphorus (RDP), dissolved organic phosphorus (DOP), total dissolved phosphorus (TDP), dissolved inorganic nitrogen (DIN).

The chlorophyll concentration was highest at point Cal 4 and lowest in the seawater scrubber outlet. At point Cal 4 also the phosphorus and nitrogen compounds were high, but highest at point Cal 2. This might indicate a higher amount of diatoms or a starting bloom.

Table 26: Nutrient concentrations determined for the samples taken on 11.02.2004

	TCHL	*Seston*	*PIP*	*POP*	*TPP*	*RDP*	*DOP*	*TDP*
	[µg L^{-1}]	[mg L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol Ll^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal 1	2.2	62.8	0.80	0.70	1.50	0.51	8.14	8.65
Cal 2	2.6	39.1	0.88	0.82	1.69	5.23	5.28	10.51
Cal 3	2.7	42.5	0.25	0.38	0.63	0.70	5.42	6.12
Cal 4	6.6	138.6	0.08	0.82	0.90	0.51	6.12	6.63
7 (Dover)	2.5	122.7	0.25	0.58	0.83	0.26	5.43	5.69
8 (Dover)	2.4	120.8	0.22	0.60	0.82	0.35	3.52	3.88
9 (Dover)	3.0	108.8	0.29	0.42	0.71	0.35	2.83	3.18
SCH1	1.4	75.1	0.10	0.36	0.45	0.35	4.20	4.55
SCH2	0.9	55.3	0.05	0.32	0.36	0.26	4.97	5.23

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	NO_2^-	NO_3^-	NH_4^+	DIN	$Si(OH)_4$
	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal 1	0.90	42.09	24.31	67.30	54.27
Cal 2	2.03	74.66	107.64	184.32	92.78
Cal 3	1.15	61.89	15.29	78.33	34.95
Cal 4	0.74	41.86	10.41	53.02	24.50
7 (Dover)	0.22	15.97	1.49	17.69	6.31
8 (Dover)	0.23	15.21	18.96	34.40	6.57
9 (Dover)	0.44	20.10	19.25	39.79	9.38
SCH1	0.33	16.41	1.53	18.26	5.63
SCH2	0.22	11.41	1.53	13.16	7.37

8.1.4 Polycyclic Aromatic Hydrocarbons

Table 69 gives the total amounts of the 16 EPA-PAHs (without naphthalene), n Table 70 the concentrations of the dissolved and the particulate are shown. The highest concentration was determined for point Cal 4: Jetee Ouest, the lowest concentration for point Cal 3 Quai de la Loire. For points Cal 2 and Cal 3 total concentrations of 267 ng L^{-1} and 354 ng L^{-1} were determined. In all cases phenanthrene was dominating and only at point 4 a higher amount of low molecular weight PAHs was found.

In Dover at all sampling points the PAH amounts were about equally high, and in the same order of magnitude as in Calais. The dominating compound was in Dover phenanthrene too. High molecular weight PAHs had extremely low contents.

The PAH contents determined for the Ecosilencer inlet and outlet are shown in Table 72. In these samples phenanthrene was dominating too. The total amount of PAHs determined at the outlet was 16-fold higher than the amount determined in the inlet water. In the outlet water the particulate fraction was about five times higher than the dissolved fraction.

To determine whether the PAHs are similarly distributed and show similar patterns a regression of the compounds was performed. The results are shown in Table 28. It can be seen that the range of the correlation coefficients is widely distributed from not significant to 0.999. Highest R^2 values were observed between the more soluble two- and three-ring compounds whereas the relation between the soluble and insoluble PAHs is lower. As this method might be influenced by great differences in concentrations of the single compounds a regression of the concentrations at the different sampling points was performed (Table 27). The difference between these two approaches is that the regression of the compounds shows high correlation coefficients if for example anthracene is high at all points where phenanthrene is low. The correlation coefficient for the regression of the sampling points reflects the relation of all compounds to each other. The regression of the sampling points delivered high correlations coefficients for all regressions. This indicates that the PAHs are similarly distributed at all points. The results of the compound regression are shown in Table 28. It can be seen that the low molecular weight PAHs are highly correlated with the remaining low molecular weight PAHs and the high molecular weight PAHs with the remaining high molecular weight PAHs. But the high molecular compounds are not correlated with the low molecular compounds. This shows that the PAH

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load of the water has a similar composition at all points, whereas the PAHs bound to particles show a different composition.

Table 27: Regression of sample points (Sampling 11.2.04). Colours are added for a better visualisation. Yellow - highly correlated, red - moderate or low correlation, dark red - no significant. correlation.

	Cal1	Cal2	Cal3	Cal4	7	8	9	SCH1	SCH2
Cal1	1	0.997	0.987	0.874	0.995	0.95	0.997	0.999	0.982
Cal2		1	0.986	0.855	0.995	0.951	0.992	0.995	0.986
Cal3			1	0.859	0.99	0.937	0.979	0.989	0.978
Cal4				1	0.833	0.822	0.884	0.865	0.786
7					1	0.946	0.987	0.997	0.993
8						1	0.947	0.947	0.932
9							1	0.995	0.97
SCH1								1	0.985
SCH2									1

Table 28: Regression of compound contents determined for the samples taken on 11.2.04. Colours are added for a better visualisation. Yellow - highly correlated, red - moderate or low correlation, dark red - no significant correlation.

	ATHY	ATHE	FLRE	PHEN	ANTH	FLUA	PYR	BaA	CHRY	BbkF	BaP	DahA	BghiP	INDE
ATHY	1	0.994	0.988	0.988	0.954	0.989	0.746	NS	0.405	NS	NS	NS	NS	NS
ATHE		1	0.995	0.995	0.967	0.995	0.753	NS	0.412	NS	NS	NS	NS	NS
FLRE			1	0.999	0.965	0.997	0.738	NS	0.404	NS	NS	NS	NS	NS
PHEN				1	0.969	0.999	0.756	NS	0.418	NS	NS	NS	NS	NS
ANTH					1	0.971	0.778	NS	0.419	NS	NS	NS	NS	NS
FLUA						1	0.779	NS	0.441	NS	NS	NS	NS	NS
PYR							1	0.497	0.821	0.418	0.403	NS	0.309	0.304
BaA								1	0.665	0.672	0.571	NS	0.435	0.417
CHRY									1	0.71	0.742	NS	0.602	0.567
BbkF										1	0.959	NS	0.913	0.835
BaP											1	NS	0.915	0.814
DahA												1	NS	NS
BghiP													1	0.957
INDE														1

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8.2 2nd sampling (March)

During this sampling the Ecosilencer was not fully operating. Problems were encountered, because the velocity of the exhaust gas was too high (17 m s^{-1}). For an optimal operation velocity should be <7 m s^{-1} to allow condensation in the funnel. Therefore, acidic droplets left the exhaust funnels. Only the exhaust gases of the four auxiliary engines were scrubbed, whereas SWS 3 was shut off, due to corrosion problems. Also auxialary engine 2 was off, but with the SWS running (Fig. 22).

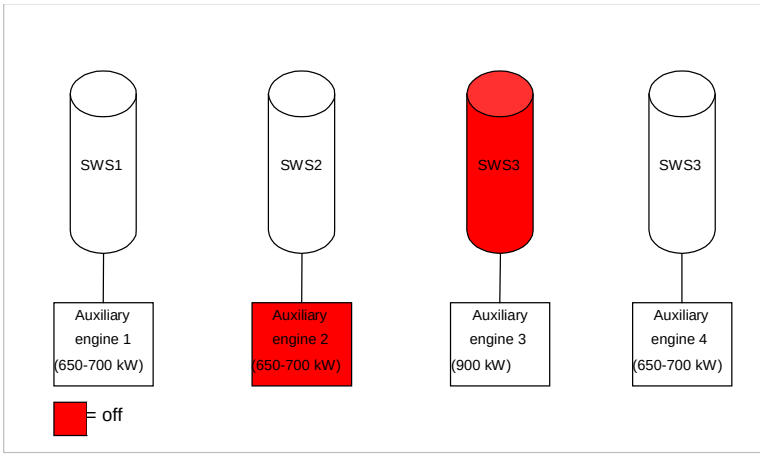

Fig. 22: The auxiliary engines and SWS running at the 24.03.04

Engine no. 2 did not produce exhaust gas, therefore the SWS 2 did not adsorb any SO_2 and others constituents of the gas. The exhaust gas of engine 3, the one with the maximum power escapes directly into the atmosphere. Thus, only half of the planned SO_2 was scavenged by the system.

8.2.1 pH, Temperature, Salinity, Conductivity, Oxygen

Table 29 shows the pH, water and air temperatures, salinity and oxygen content determined for the samples taken in Calais on 23.3.2004. Values measured at points Cal 1, Cal 2 and Cal 4 are nearly the same with the highest pH value measured at point Cal 4 and the highest salinity measured at point Cal 2. Point Cal 3 is in all cases an exception. At this point an unusually high pH value and oxygen content were measured. Also a lower temperature and salinity were observed.

Table 29: Air and water temperature [°C], salinity [PSU], pH value and oxygen [mg L^{-1}] during sampling in Calais harbour on 23.3.2004

		temp. air [°C]	temp. water [°C]	salinity [PSU]	pH	oxygen [mg L^{-1}]
Cal 1	Quai en eau profonde	8.6	8.5	31.2	8.42	9.85
Cal 2	Quai de service	8.1	8.5	31.7	8.50	9.79
Cal 3	Quai de la Loire	9.4	7.7	27.5	9.35	>20
Cal 4	Jetee ouest	8.1	8.5	31.5	8.63	9.87

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All samples in Calais were taken between 16:00 and 18:30 (CET). According to Table 8 high tide was at 14:21 and therefore samples were taken at ebb tide.

Table 30 shows the pH, water and air temperatures, salinities and oxygen contents determined for the samples taken in Dover on 24.03.2004. The samples from points 5 and 6 were taken between 8:40 and 10:00 (Table 9) and therefore shortly after low tide (Table 8). Samples at point 7, 8 and 9 were taken between 13:15 and 13:35 and therefore quite exactly at high tide. The lowest temperature was measured at point 6 the other values determined for this point are about the same as those measured close to the „Pride of kent“. The sample take at the beach at point 5 had the lowest salinity and the lowest pH.

Table 30: Air and water temperatures [°C], salinity [PSU], pH value and oxygen [mg L^{-1}] during sampling in Dover harbour on 24.3.2004

Dover		temp. air [°C]	temp. water [°C]	salinity [PSU]	pH	oxygen [mg L^{-1}]
Point 5	Churchill Hotel Beach	9.0	11.0	27.0	7.68	9.52
Point 6	Prince of Wales pier	7.4	8.9	34.3	7.86	10.1
Point 7	Back of „Pride of kent“	12.3	8.8	34.2	7.95	
Point 8	Middle of „Pride of kent“	12.3	8.8	34.4	7.95	
Point 9	Front of „Pride of kent“	12.3	8.8	34.4	8.00	

Table 31 shows the pH, the salinities and the temperatures measured inside the seawater scrubber system. Looking at the inlet samples, the temperature was highest inside the Channel (15.2°C). The lowest salinity was measured in Calais (32.9) and the lowest pH (7.72) in Dover. If these values are compared with the values at the outlet it can be seen that the salinity was slightly increased and the temperature was raised by about 2 °C to 3 °C. The pH was lowered in all cases. The strongest reduction was observed in the channel where the difference between inlet and outlet pH was 1.16 pH units whereas in Calais and in Dover it was 0.66 and 0.43, respectively.

Table 31: Water temperature [°C], salinity [PSU], pH value and oxygen [mg L^{-1}] during sampling on the “Pride of Kent” on 24.3.2004

		temp. water [°C]	salinity [PSU]	pH
SD1	seawater inlet Dover	10.7	34.2	7.72
SD2	seawater outlet Dover	14.8	34.6	7.29
SCH1	seawater inlet Channel	15.2	34.9	7.94
SCH2	seawater outlet Channel	17.1	35.2	6.78
SCH3	outlet from US filter	27.6	35.5	2.73
SCH4	to settling tank	28.8	35.4	2.86
SCH5	inlet to US filter	27.9	35.2	2.82
SCH6	return from Ecosilencer	28.0	35.2	2.78
SCH7	top of settling tank	27.2	33.5	2.83
SCH8	bottom of settling tank	23.0	34.9	2.83
SC1	seawater inlet Calais	9.5	32.9	8.00
SC2	seawater outlet Calais	12.8	32.9	7.34

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The values determined for the samples taken from the remaining seawater scrubber points show, with the exception of the settling tank, no change in salinity. Inside the settling tank the salinity was lower perhaps because the water remains there for a while and therefore water from different water bodies is mixed. The remaining time of the water inside the settling tank might also be an explanation why there the pH is higher than pH 3 as in comparison to the remaining seawater scrubber points, where it is lower than 3. Although the effluent water had a significantly lower pH than the inflowing water, no pH change in the harbour or close to the “Pride of Kent” was measured. Additionally there was no pH change observable inside the harbour between the first sampling where the Ecosilencer was not running and the second sampling.

8.2.2 Metals and Sulphate

Sulphate, transition and earth metal concentrations of the harbour and the Ecosilencer samples taken on 23/24.03.2004 are given in Table 32. Inside the ports a copper concentration of 220 ppb in Calais at point Cal 1 and a zinc concentration of 53 ppb at point 9 in Dover were observed. Sulphate concentrations were highest in Dover at the Prince of Wales Pier and at Terminal 4 (back of “Pride of Kent”, Point 9). The samples taken in the middle (point 8) and at the front (point 7) of the „Pride of Kent“ show lower earth metal and sulphate conentents than the other samples.

Inside the seawater scrubber system the highest transition metal contents were determined for the samples taken from the tube to the settling tank and inside the settling tank. Additionally, high copper and zinc concentrations were found at the inlet to the US filter. Except for iron (789 ppb) no metals could be detected directly after the Ecosilencer. This indicates that most metals are leached from the tubing due to the low pH and do not originate from the fluegas scrubbing process itself. At the outlet of the US filter only vanadium (183 ppb) was determined and in the SWS outlet sample taken in the Channel and in Dover, zinc (138 ppb and 537 ppb) was detected. Inside the seawater scrubber system highest transient metal concentrations were found at the inlet to and inside the settling tank. This indicates that most of the metals are bound to particles or are particulates themselves and are therefore effectively removed from the system.

Sulphate concentrations did show an increase inside the SWS directly after the Ecosilencer but this increase was diluted to the SWS inlet sulphate level before it left the „Pride of Kent“. Inside the harbours the sulphate concentrations are at about the same level as the effluent concentrations but due to different salinity values they vary within a range of 1500 and 3350 ppm.

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Table 32: Sulphate, earth and transition metal contents determined for the samples taken in July

		Cal 1	Cal 2	Cal 3	Cal 4	5	6	7	8	9	SD1	SD2	SCH2	SCH1	SCH3	SCH4	SCH5	SCH6	SCH7	SCH8	SC1	SC2
Ba	ppb	18	20	22	18	23	19	18	15	19	16	17	16	21	18	34	19	19	24	26	18	19
Ca	ppm	382	356	348	380	341	398	327	279	371	395	397	405	406	411	434	404	396	396	562	381	370
Cd	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Co	ppb	-	-	-	-	-	-	-	8	-	-	-	-	-	-	-	-	-	-	-	-	-
Cr	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	264	-	-	-	-	-	-
Cu	ppb	220	-	-	-	-	-	-	-	-	129	129	-	-	-	7089	10978	-	273	2127	-	-
Fe	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	1051	5283	892	789	1508	-	-	-
K	ppm	352	345	314	366	288	398	340	297	381	397	384	428	426	434	437	422	419	405	424	388	367
Li	ppb	164	158	147	165	140	178	150	128	169	188	188	187	185	185	185	183	180	175	183	172	166
Mg	ppm	1154	1091	1007	1161	980	1251	1028	883	1173	1213	1202	1278	1278	1290	1289	1272	1245	1207	1255	1189	1149
Mn	ppb	-	-	-	-	-	-	-	-	-	-	20	-	-	-	72	-	-	-	332	-	-
Mo	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	403	-	-
Ni	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	277	-	-	-	1076	-	-
Pb	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
SO4	ppm	2619	2625	2307	2628	2277	2920	2342	1942	2955	2949	2962	2990	3052	3342	3380	3359	3550	3235	3419	2920	2938
Sr	ppb	7220	6829	6345	7202	6160	7730	6410	5490	7308	7987	8024	8031	7953	8074	8193	7950	7830	7616	8491	7487	7151
V	ppb	-	-	-	-	-	-	-	-	-	-	-	-	-	183	320	-	-	-	-	-	-
Zn	ppb	-	-	-	-	-	-	-	-	53	-	537	-	138	-	1033	1461	655	414	98	-	-

For a better visualisation and a better estimate of the SWS influence a comparison between the sulphate, transition and earth metal concentration determined for the SWS inlet and outlet is show in Figs. 22 to 28 comparing the inlet and outlet samples taken in March and February. Samples taken on 11.02.2004 are marked, because during this sampling the seawater scrubber was not running. During the sampling on 24.03.2004 copper was found in inlet and outlet samples taken in Dover. In both samples the copper concentration was the same. In Dover also manganese was found, but only in the outlet effluent. In all outlet but not in the inlet samples except in Calais on 24.03.2004 zinc was determined. Earth metals were all, within the accuracy of the measurements, equally concentrated in the inlet and outlet samples, only barium seems to be slightly increased, when the SWS is running.

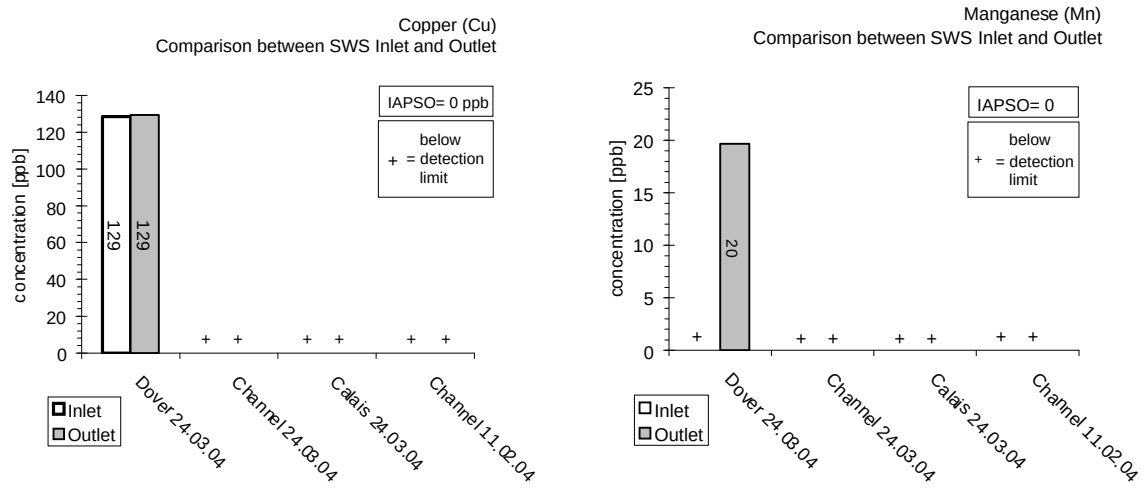

Fig. 23: Left: Copper content [ppb]. Right: Manganese content [ppb] determined for Ecosilencer inlet and outlet samples taken in Calais, Dover and the Channel on 23/24.03.2004 and on 11.02.2004. IAPSO: Atlantic water salinity standard.

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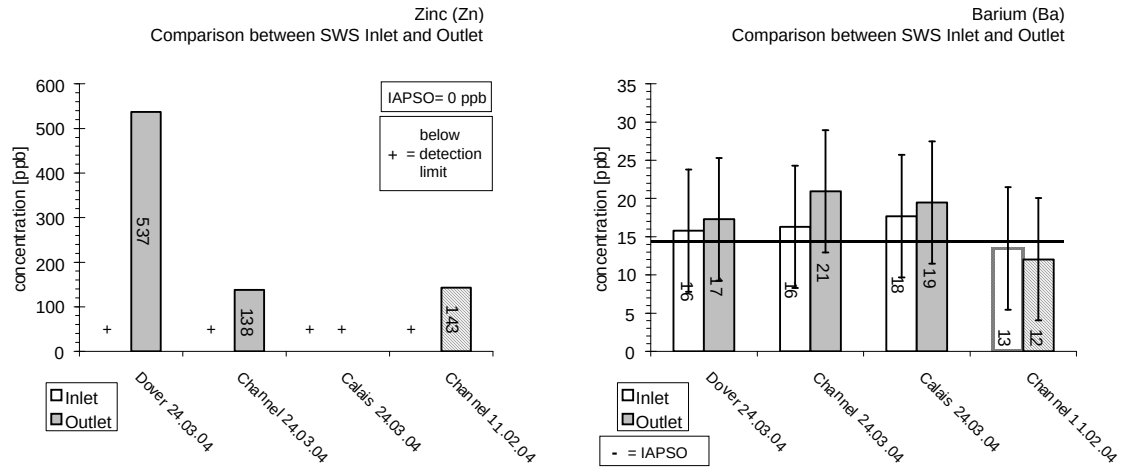

Fig. 24: Left: Zinc content [ppb]. Right: Barium content [ppb] determined for Ecosilencer inlet and outlet samples taken in Calais, Dover and the Channel on 23/24.03.2004 and on 11.02.2004. IAPSO: Atlantic water salinity standard.

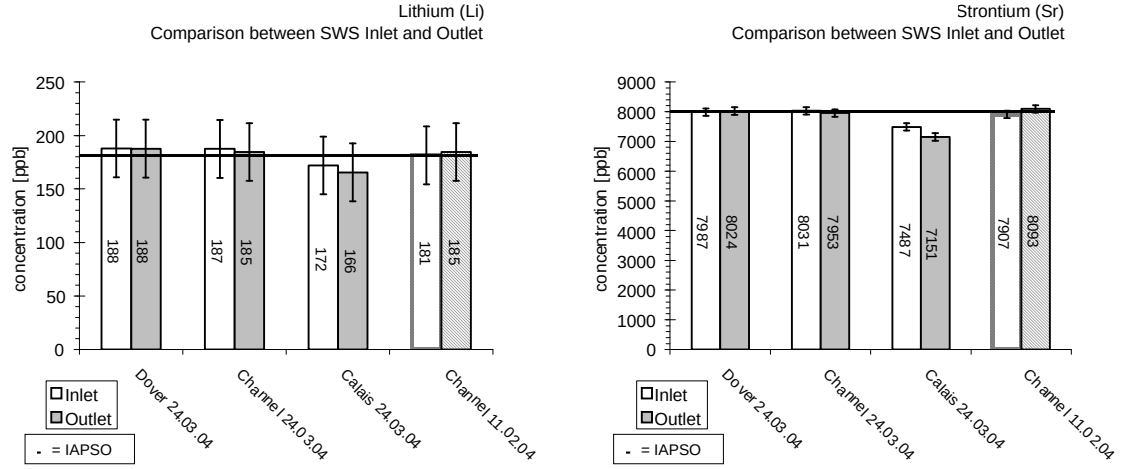

Fig. 25: Left: Lithium content [ppb]. Right: Strontium content [ppb] determined for Ecosilencer inlet and outlet samples taken in Calais, Dover and the Channel on 23/24.03.2004 and on 11.02.2004. IAPSO: Atlantic water salinity standard.

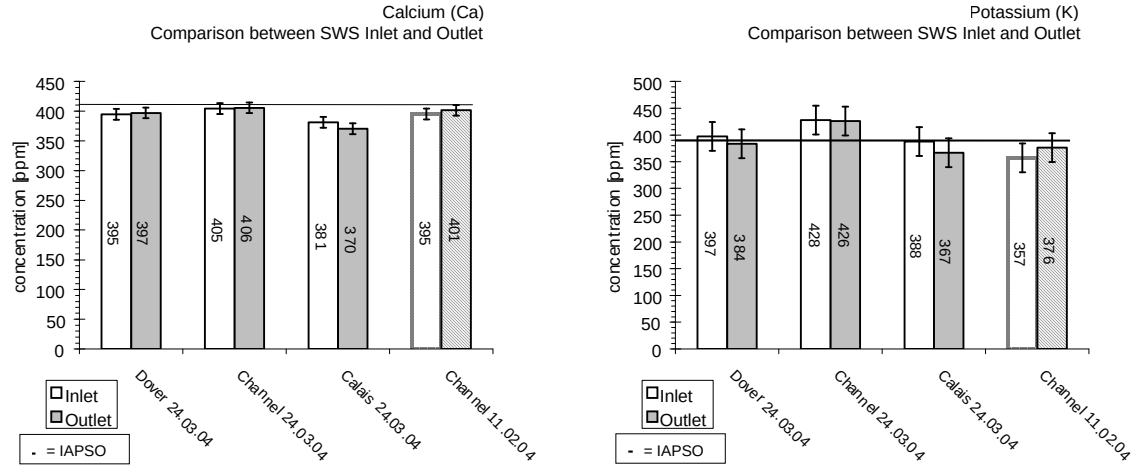

Fig. 26: Left: Calcium content [ppm]. Right: Potassium content [ppm] determined for Ecosilencer inlet and outlet samples taken in Calais, Dover and the Channel on 23/24.03.2004 and on 11.02.2004. IAPSO: Atlantic water salinity standard.

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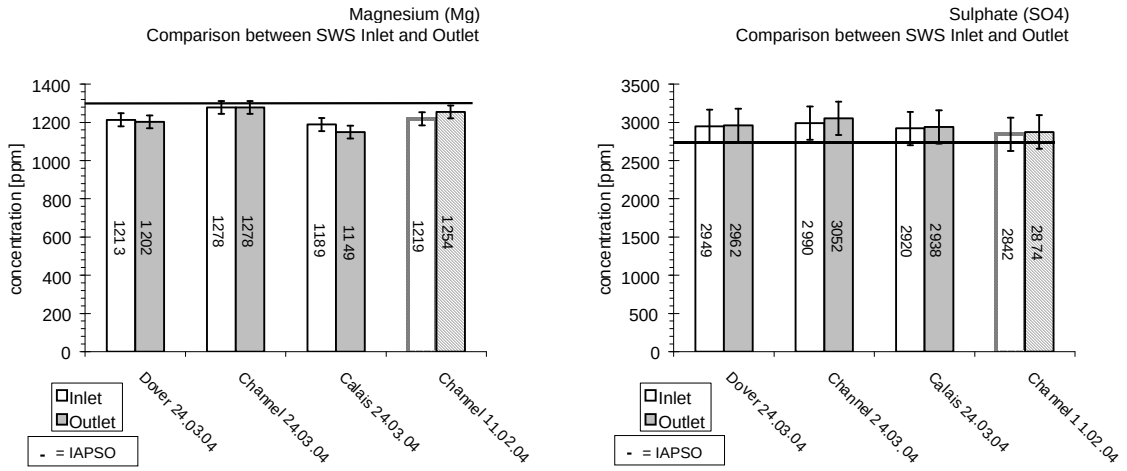

Fig. 27: Left: Magnesium content [ppb]. Right: Sulphate content [ppb] determined for Ecosilencer inlet and outlet samples taken in Calais, Dover and the Channel on 23/24.03.2004 and on 11.02.2004. IAPSO: Atlantic water salinity standard.

8.2.3 Nutrients

Table 26 shows the nutrient and seston contents determined for the samples taken in March. In Calais the highest seston content was observed at point Cal 2 (50.9 mg L^{-1}) where about double the content of the remaining points was observed. Sampling point 5 was situated at a sandy beach therefore the seston content was higher (80.9 mg l^{-1}) in comparison to the sample taken at the Prince of Wales pier where the seston content was comparable to those measured in Calais. On board of the „Pride of Kent“ the highest contents where not observed inside the settling tank as expected, but in the outlet of the US filter (132.0 mg L^{-1}). Inside the pipe which leads the water to the settling tank also high particle contents where observed. Looking at the inlet and the outlet samples it can be seen, that the highest seston contents were observed in the inlet sample taken in Calais (262.6 mg L^{-1}). This might be an effect of the berthing, where the screws whirl up a lot of sediment, which then might be sucked into the ships cooling cycle. In Calais and Dover the seston contents in the outlet are lower than those observed in the inlet. That shows that the clean-up system inside the ship (cyclones, settling tank and US filter) worked and removed these particles. It also explains the high content measured at point SCH4 where the removed particles pass by.

Looking at the RDP, DOP and TDP values it can be seen that they are quite the same in Dover and Calais. Only at point Cal 3 where the algal bloom was observed nearly doubled TDP concentrations were determined. At this point also the DIN concentrations were very high and only inside the settling tank higher concentrations were measured. In both samples these high concentrations are due to by high ammonia values; 33.05 µmol L^{-1} at point Cal 3 and 76.66 µmol L^{-1} at point SCH8 were observed, whereas at the remaining points the concentrations varied between 1.34 and 12.81 µmol L^{-1}. A nitrate increase in the outlet samples in comparison to the inlet samples was only observed in Dover and inside the Channel. In Calais the inlet sample contained more nitrate (20.47 µmol L^{-1}) than the outlet

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sample (18.30 µmol L^{-1}), but nitrite concentrations were higher in the outlet samples in Calais and the Channel and equally high in the inlet and outlet samples in Dover.

Silicate concentrations were also highest in the sample taken from the settling tank (78.53 µmol L^{-1}). Inside the ports of Dover and Calais the highest concentrations were again measured at point Cal 3 and point 5. At point 5 the high concentration originates from the sand at the beach and at point Cal 3 centric diatoms were observed which are mainly built up by silicate.

Inside the seawater scrubber system high nitrate concentrations were observed, as expected, behind the Ecosilencer (19.38 µmol L^{-1}). At the following points the nitrate concentrations were reduced to 17.3 µmol L^{-1} at the inlet and 14.73 µmol L^{-1} at the outlet of the US filter. In the overboard discharge the remaining nitrate concentration was only 8.55 µmol L^{-1}. In contrary to the reduction of nitrate, the reduced nitrogen compounds nitrite and ammonia increased slightly.

Table 33: Nutrient concentrations determined for the samples taken on 24.03.2004

samp. point	Seston	RDP	DOP	TDP	NO_2^-	NO_3^-	NH_4^+	DIN	$Si(OH)_4$
	[mg L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal1	35.6	0.18	4.43	4.60	0.83	24.37	-	-	18.41
Cal2	50.9	0.66	2.71	3.37	0.64	20.97	12.81	34.42	14.75
Cal3	23.7	2.20	4.80	7.00	1.38	18.92	33.05	53.35	25.27
Cal4	22.2	0.42	3.88	4.30	0.78	25.63	8.33	34.74	10.89
5	80.9	1.30	3.15	4.45	0.22	22.57	1.34	24.12	38.23
6	36.7	0.18	4.89	5.07	0.32	20.08	4.11	24.50	7.04
SD1	47.2	0.18	-	-	0.20	14.72	-	-	17.81
SD2	41.5	0.14	-	-	0.20	18.67	-	-	15.15
SCH1	4.6	0.08	-	-	0.22	7.89	-	-	4.08
SCH2	8.3	0.04	-	-	2.97	8.55	-	-	18.22
SCH3	132.0	1.21	-	-	0.21	14.73	3.14	18.07	25.89
SCH4	118.5	0.79	-	-	1.62	13.38	6.11	21.11	16.11
SCH5	25.9	0.77	-	-	0.17	17.30	3.63	21.11	9.37
SCH6	55.3	0.35	-	-	0.05	19.38	3.01	22.44	12.41
SCH7	23.0	0.79	-	-	0.09	26.17	8.21	34.47	20.86
SCH8	39.0	0.12	-	-	1.30	11.17	64.19	76.66	78.53
SC1	262.6	0.11	-	-	0.60	20.47	8.55	29.62	9.29
SC2	49.9	0.19	-	-	1.30	18.30	6.92	26.53	8.82

8.2.4 Polycyclic Aromatic Hydrocarbons

The total PAH contents determined for the Calais port samples are shown in Table 69. The highest amount was measured at point Cal 3. At this point the PAH content was about double the content observed at the other points. The high content might originate from the high amount of planktic organisms observed at that point. PAHs might adsorb onto the surface of these organisms and thus remain for a longer time in the water column. Also the PAHs might have been taken up actively from the water resulting in an enrichment of PAHs in the organisms. The contents observed at the remaining points are about as high as those determined for the first sampling. In all samples phenanthrene was the dominating compound. High contents were also determined for pyrene and fluoranthene.

The PAH contents determined for the samples taken in Dover are shown in Table 70. In all samples phenanthrene was the dominating compound too. In front of the “Pride of Kent”, phenanthrene was

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reduced and anthracene, pyrene and fluoranthene were slightly increased. At Point 5 the particulate PAH fraction was higher than at the other points. This is also underlined by the high seston contents determined for that point, originating from the sandy beach. Looking at the total PAH amounts, the lowest contents were found at point 9 (front of „Pride of Kent“) and the highest at point 6 (Prince of Wales Pier). Close to this point is a catamaran berth. These ships blow their flue gas directly into the screw water. Additionally at this point there are only low current speeds and hence a reduced water exchange. The particles might remain for a longer time close to the surface and are therefore higher contaminated with PAHs.

The results of the PAH-extraction from the Ecosilencer samples which were taken in the Channel during normal operation mode of the „Pride of Kent“ are shown in Table 70 and Table 72. Taking the inlet and the outlet into closer view it can be seen that the PAH content is about 10 times higher in the outlet water than in the inlet water. The PAH composition inside the system is about the same at all points, with phenanthrene dominating and high amounts of chrysene and pyrene also. The highest contents were found in the tube going to the settling tank and at the bottom of the settling tank. This is not surprising, as contaminated particles are enriched in the cyclones and transferred to the settling tank. The samples taken before and after the US filter, which also should remove particles and oil from the water, show that the filter system worked. The total PAH content was reduced from 15151 ng L^{-1} to 12502 ng L^{-1}. Within this reduction not only the particulate PAHs are included but also the dissolved ones. The highest PAH contents were determined for the sample taken from the bottom of the settling tank.

Origin of PAHs

Tables 34 to 37 and Fig. 28 show the calculated indices, which could be used to determine the origin of the PAHs. A description of the basics of these indices is given in 5.4.3. Nearly all results, even those that are not significant, show a petrogenic origin. The exceptions are for Flu/Pyr for all samples taken in February without sample Cal 4, and for the second sampling for all samples with exception of Cal 3. For Phe/Anth the exceptions were in February point 8 and in March point 9, and for Chr/BaA the sample taken in February at point Cal 3 and in February at point 7.

Table 34: Indices for the determination of the origin of the PAHs (samples 11.02.04)

	Feb Cal 1	Feb Cal 2	Feb Cal 3	Feb Cal 4	Feb 7	Feb 8	Feb 9	Feb SCH1	Feb SCH2
PHEN/ANTH	11.6	10.8	11.9	13.4	11.4	3.3	11.7	12.4	14.4
FLUA/PYR	1.2	1.5	1.7	0.5	1.4	1.3	1.1	1.1	3.8
CHRY/BaA	1.8	1.9	0.5	2.9	0.7	1.7	1.9	1.3	4.6

Table 35: Indices for the determination of the origin of the PAHs (harbour samples 24.03.04)

	March Cal 1	March Cal 2	March Cal 3	March Cal 4	March 5	March 6	March 7	March 8	March 9
PHEN/ANTH	15.8	15.1	10.0	14.4	15.1	20.2	14.6	15.7	3.5
FLUA/PYR	0.5	0.8	1.5	0.8	0.4	0.5	0.8	0.6	1.1
CHRY/BaA	3.1	2.9	1.2	2.8	2.5	1.2	1.8	3.3	2.9

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For a better visualisation, the Phe/Anth and Flu/Pyr quotients are plotted in Fig. 28 and in a more detailed version for the samples taken on board of the „Pride of Kent“ in Fig. 29. In these figures the indices for coal tar and shale oil are also shown. These data underline what the indices alone already showed. Most of the samples are to bed found in the border region between petrogenic and pyrolytic origins. Only the Ecosilencer samples (without the samples from the inlet) are clearly of petrogenic origin. These results are partially surprising. On the one hand no clear results were expected for the harbour samples, because the samples were taken in harbours with high ship traffic, which would explain the petrogenic origin. Additionally there are cities and car routes nearby, therefore also PAHs with a pyrolytic origin, resulting in an inhomogeneous mixture of PAHs from different origins, creating no clearly defined indices. On the other hand it is surprising, because the samples taken inside the seawater scrubber, should clearly indicate pyrolytic origin. The reason that this is not the case might be the incomplete combustion of the fuel and therefore the high amounts of “petrogenic” PAHs.

Table 36: Indices for the determination of the origin of the PAHs (harbour Ecosilencer samples 24.03.04)

	March SD1	March SD2	March SC1	March SC2
PHEN/ANTH	16.0	34.5	14.1	37.7
FLUA/PYR	0.4	0.6	0.9	0.4
CHRY/BaA	3.7	3.5	2.0	2.7

Table 37: Indices for the determination of the origin of the PAHs (Channel of Dover Ecosilencer samples 24.03.04)

	March SCH1	March SCH2	March SCH3	March SCH4	March SCH5	March SCH6	March SCH7	March SCH8
PHEN/ANTH	14.6	30.1	57.9	42.9	42.1	50.9	54.2	41.7
FLUA/PYR	0.8	0.5	0.5	0.3	0.5	0.4	0.5	0.4
CHRY/BaA	2.2	4.1	2.8	2.6	3.3	3.1	2.7	2.7

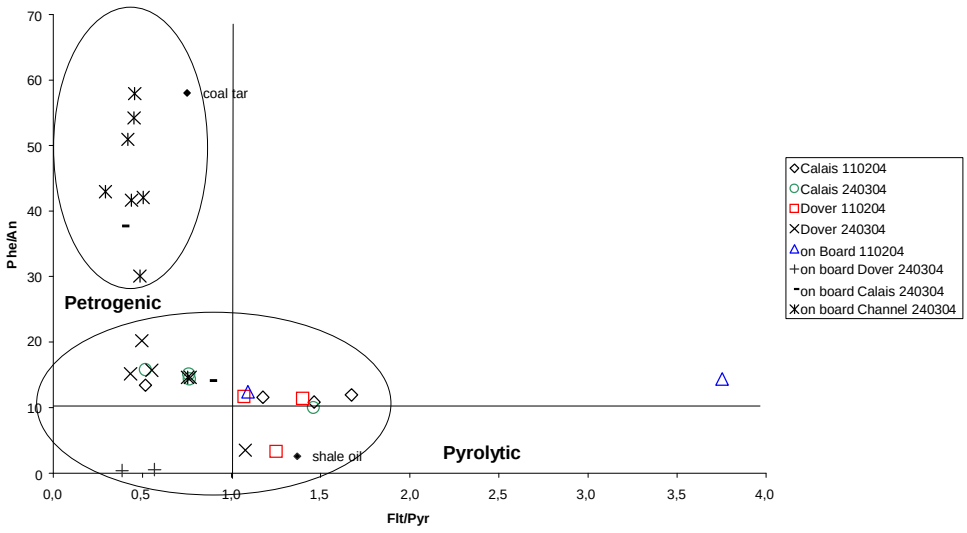

Fig. 28: Plot of isomeric phenanthrene/anthracene ratios against fluoranthene/pyrene ratios for all samples taken in February and March

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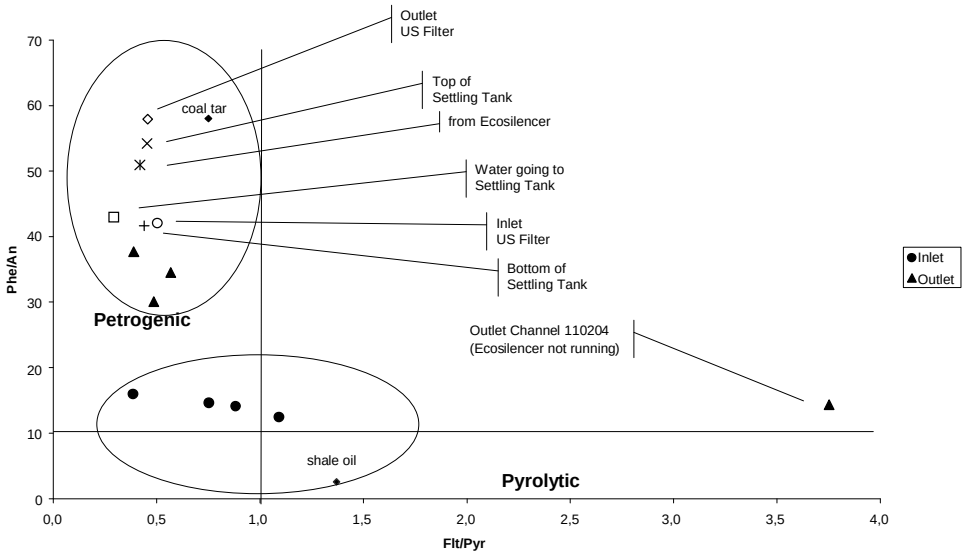

Fig. 29: Plot of isomeric phenanthrene/anthracene ratios against fluoranthene/pyrene ratios for the seawater scrubber samples taken in February and March.

To determine whether all PAHs in the samples originate from one source, a linear regression analysis of all substances with each other was performed. If a regression coefficient of 1,000 is observed, all points are lying on one line. That means, that in all samples the same relationship of the observed PAH in relation to the remaining PAHs is present. If all regressions show an R^2 of 1 all samples have the same composition and this would indicate that they all originate from one source. The advantage of this method is that the content has no influence on this calculation.

Table 38: Regression chart for the analysis of the sampling points (Sampling March). Colours are added for a better visualisation. Yellow highly correlated, orange and red moderate or low correlation, dark red no significant. correlation.

	Cal1	Cal2	Cal3	Cal4	5	6	7	8	9	SD1	SD2	SCH1	SCH2	SCH3	SCH4	SCH5	SCH6	SCH7	SCH8	SC1	SC2	
Cal1	1	0.989	0.928	0.986	0.939	0.969	0.984	0.996	0.734	0.999	0.982	0.966	0.985	0.991	0.927	0.98	0.982	0.977	0.954	0.973	0.982	Cal1
Cal2		1	0.953	0.98	0.894	0.953	0.993	0.978	0.732	0.331	0.901	0.985	0.968	0.978	0.876	0.963	0.959	0.949	0.91	0.992	0.954	Cal2
Cal3			1	0.953	0.864	0.916	0.947	0.925	0.829	0.342	0.791	0.929	0.892	0.906	0.808	0.894	0.885	0.885	0.861	0.949	0.883	Cal3
Cal4				1	0.943	0.974	0.978	0.989	0.795	0.411	0.833	0.956	0.961	0.967	0.908	0.955	0.957	0.959	0.947	0.966	0.963	Cal4
5					1	0.955	0.883	0.96	0.785	0.604	0.697	0.837	0.941	0.939	0.977	0.94	0.953	0.969	0.991	0.856	0.969	5
6						1	0.958	0.971	0.75	0.406	0.82	0.933	0.943	0.962	0.914	0.943	0.949	0.956	0.948	0.943	0.96	6
7							1	0.971	0.715	0.292	0.916	0.994	0.949	0.965	0.852	0.943	0.94	0.931	0.896	0.996	0.938	7
8								1	0.755	0.447	0.843	0.946	0.987	0.988	0.946	0.982	0.985	0.985	0.972	0.955	0.988	8
9									1	0.541	0.436	0.683	0.693	0.69	0.702	0.687	0.692	0.714	0.741	0.7	0.712	9
SD1										1	0.119	0.238	0.456	0.418	0.634	0.46	0.478	0.513	0.587	0.26	0.5	SD1
SD2											1	0.933	0.854	0.874	0.701	0.849	0.838	0.809	0.738	0.927	0.818	SD2
SCH1												1	0.923	0.943	0.806	0.915	0.911	0.897	0.852	0.996	0.906	SCH1
SCH2													1	0.995	0.956	0.998	0.998	0.993	0.967	0.936	0.993	SCH2
SCH3														1	0.945	0.996	0.995	0.99	0.961	0.954	0.992	SCH3
SCH4															1	0.957	0.969	0.979	0.99	0.824	0.978	SCH4
SCH5																1	0.998	0.994	0.967	0.931	0.993	SCH5
SCH6																	1	0.998	0.977	0.925	0.998	SCH6
SCH7																		1	0.988	0.913	0.999	SCH7
SCH8																			1	0.87	0.986	SCH8
SC1																				1	0.919	SC1
SC2																					1	SC2

The results for the regressions are shown in Table 38 and Table 39. The regressions of the PAHs among each other show a high correlation. The only two samples that show a different composition

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are the samples taken from the inlet inside the harbour of Dover and that one taken in Dover at the front of the „Pride of Kent“.

Table 39: Regression of compound contents determined for the Samples taken on 24.03.04. Colours are added for a better visualisation. Yellow - highly correlated, red - moderate or low correlation, dark red - no significant. correlation.

	ATHY	ATHE	FLRE	PHEN	ANTH	FLUA	PYR	BaA	CHRY	BbkF	BaP	DahA	BghiP	INDE
ATHY	1	0.945	0.948	0.936	0.942	0.913	0.893	0.891	0.909	0.873	0.927	0.878	0.837	0.808
ATHE		1	0.988	0.988	0.955	0.953	0.956	0.959	0.971	0.911	0.989	0.933	0.881	0.836
FLRE			1	0.987	0.955	0.937	0.92	0.923	0.95	0.883	0.982	0.9	0.846	0.801
PHEN				1	0.975	0.966	0.952	0.949	0.967	0.925	0.984	0.937	0.897	0.857
ANTH					1	0.964	0.953	0.946	0.964	0.943	0.962	0.947	0.916	0.889
FLUA						1	0.972	0.955	0.961	0.985	0.951	0.97	0.971	0.951
PYR							1	0.995	0.989	0.976	0.964	0.994	0.964	0.936
BaA								1	0.993	0.955	0.974	0.988	0.939	0.905
CHRY									1	0.951	0.988	0.981	0.93	0.894
BbkF										1	0.918	0.984	0.997	0.986
BaP											1	0.95	0.888	0.884
DahA												1	0.977	0.955
BghiP													1	0.955
INDE														1

Additionally to the regression analysis a principal component analysis was performed. The results are shown in Fig. 30. The feature vector is shown in Table 40. Eigenvector 1 is responsible for 70.6 % and eigenvector 2 is responsible for 19.6 % which sums up to 90.2 % of the total variance. According to Fig. 30 the samples can be divided into three groups. One is made up by one sample taken at point Cal 3 and is characterized by a high positive value for eigenvector 1 and a negative value for eigenvector 2. At Cal 3 high contents of low molecular weight PAHs were observed. This is shown by the negative value for eigenvector 2. Eigenvector 1 mainly corresponds to the overall content and is positive for high amounts and negative for low contents. The second group shows negative values for eigenvector 1 and values close to zero for eigenvector 2.This group includes the samples taken in Calais (also from the seawater scrubber inlet) and the samples taken in front of the “Pride of Kent”. These samples are characterized by low contents of phenanthrene and high molecular weight PAH contents. The third group contains the remaining samples taken in Dover. These samples show high contents of those high molecular weight PAHs that are positive in the feature vector.

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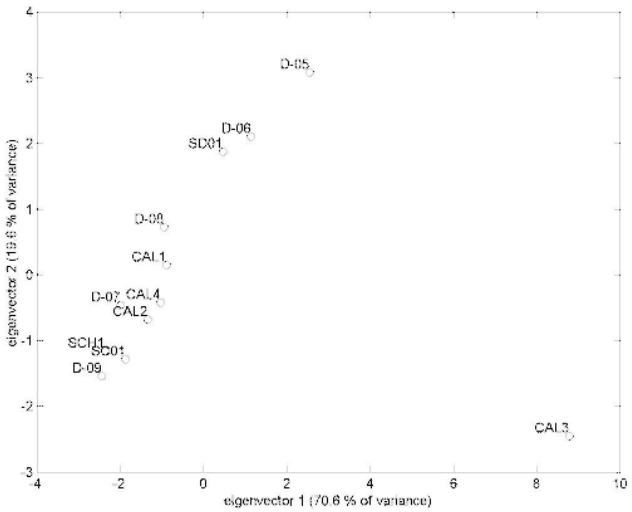

Fig. 30: Results of the PCA of the harbour samples

Table 40: Feature vector for the PCA of the harbour samples

	70.6 % (14.0)	19.6 % (14.0)
acenaphthylene	0.28	-0.25
acenaphthene	0.23	-0.36
fluorene	0.27	-0.31
phenanthrene	0.26	0.06
anthracene	0.27	-0.29
fluoranthene	0.30	-0.14
pyrene	0.20	0.46
benz[*a*]anthracene	0.30	0.22
chrysene	0.15	0.41
benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0.30	0.08
benzo[*a*]pyrene	0.23	0.37
dibenz[*a,h*]anthracene	0.30	-0.07
benzo[*ghi*]perylene	0.30	0.16
indeno(1,2,3,*c,d*)pyrene	0.31	-0.05

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8.3 3rd sampling (July)

8.3.1 pH, salinity and temperature

During this sampling additional samples to those taken on board of the “Pride of Kent” and from the harbour walls were taken. The high and low water dates and the sampling times are given in Table 8 andTable 9. The pH, salinity and temperature data for this sampling are shown in Table 41. The air temperatures were higher during the sampling on the boat than during the sampling from the quay walls. The water temperature was highest at Point C5 and lowest at point Cal 3 “Quai de la Loire”. The salinity was lower in those samples taken close to the shore than in those taken inside the harbour and lowest at point Cal 1 and Cal 3. Both points are enclosed by harbour walls and water exchange is only possible from one side. Therefore the water has a more brackish character. This is mainly due to the higher buoyancy of water with lower salinity and higher temperatures compared to the cooler water in deeper layers. Because of high temperatures and less wind this stratification is enforced in summer and often lasts until fall. From point C5 to C700 a slight increase in pH was observed. As the salinity also increased this might be a salinity effect. The temperature at point C5 was about 1 °C higher than at point C50. This might be an effect of the cooling water which was approximately 3 °C higher than the inlet water. The temperature, salinity and pH data observed in the harbour of Dover are shown in Table 42. The air temperature was constant during the sampling as well as the water temperature and the salinity. The pH varied between 8.30 at point D0 and maximal 8.38 at point D700.

Table 41: Temperature, salinity and pH data measured at the different sampling points in Calais harbour

point	Temp [°C] air	Temp [°C] water	Sal [PSU]	pH
Cal 1	15.0	17.0	29	7.69
Cal 2	15.2	17.1	31	8.07
Cal 3	15.8	16.5	29	8.28
Cal 4	17.3	16.9	32	8.22
C5	18.0	18.2	34	8.28
C50	18.0	17.1	34	8.29
C350	18.0	17.2	34	8.31
C700	18.0	17.5	35	8.37

Table 42: Temperature, salinity and pH data measured at the different sampling points in Dover harbour

point	Temp [°C] (air)	Temp [°C] water	Sal [PSU]	pH
D0	16.4	15.9	34	8.30
D5	16.4	15.9	34	8.35
D50	16.4	15.9	34	8.35
D350	16.4	15.9	34	8.35
D700	16.4	15.9	34	8.38
Dov 1	16.4	15.9	34	8.35
Dov 2	16.4	15.9	34	8.35
Dov 3	16.4	15.9	34	8.35
Dov 4	16.4	15.9	34	8.37

The water temperature, the salinity and the pH values for the samples taken inside the „Pride of Kent“ are shown in Table 43. Comparing the inlet and outlet samples in all cases the effluent temperature

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was about 3 °C higher than that of the inlet water and the pH was lower by about 1.5 pH units. The salinity was nearly constant with 35 PSU at all points. Inside the seawater scrubber the lowest pH was found at point SCH6 behind the Ecosilencer. At the US filter inlet and outlet the pH was already 0.14 pH units higher and in the outlet after dilution with the cooling water the pH was nearly neutral.

Table 43: Seawater scrubber temperatures, salinities and pH data

point	Temp [°C] water	Sal [PSU]	pH
SD1	17.8	35.0	8.38
SD2	20.7	34.0	6.87
SCH1	17.4	35.0	8.44
SCH2	20.2	35.0	6.99
SCH3	36.7	34.5	3.14
SCH5	36.0	35.0	3.13
SCH6	37.0	35.0	3.09
SC1	18.2	35.0	8.16
SC2	20.9	35.0	6.82

8.3.2 Nutrients

Table 44 shows the chlorophyll, seston and nutrient data determined for the samples taken in July. In Dover only at point D5 the chlorophyll content was high enough to be determined. In Calais the contents varied between 11.7 µg L^{-1} and 33.1 µg L^{-1}. The highest content was observed at the berth in front of the “Pride of Kent”. The seawater scrubber inlet and outlet samples taken in Calais are about equally concentrated as those taken from the transect sampling points. The chlorophyll contents determined for the remaining seawater scrubber samples are all within the same order of magnitude. Nearly all seston contents laid between 50 and 65 mg L^{-1}. Only at point C5 a higher seston content of 86.7 µg L^{-1} was measured. As at this point the chlorophyll content was high too the seston content most probably originated from a high plankton abundance. Inside the seawater scrubber system the highest seston content was measured in the outlet of the US filter. Comparing the inlet and outlet samples only in Dover an increased seston content was observed in the outlet.

The determined RDP, DOP and TDP concentrations show no significant trend and varied between 0.33 - 5.07 µmol L^{-1} (RDP) 0.11 - 2.41 µmol L^{-1} (DOP) and 1.12 -2.96 µmol L^{-1}. The highest RDP value was measured at point Cal 3. At this point also the nitrate, nitrite, ammonium and silicate concentrations were high. As no significantly higher seston or chlorophyll contents were determined for that point it can be stated that at this point an algal bloom started. Comparing the determined concentrations of both harbours it can be seen that in Calais the DIN and silicate concentrations were generally higher than those in Dover.

Taking the seawater scrubber system samples into closer view, it can be seen that the highest nitrate concentration was observed behind the Ecosilencer. According to the high ammonia concentration determined for the US-filter sample the highest DIN concentration was observed at point SCH5. All

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outlet samples showed a higher DIN concentration than the inlet sample. This is mainly due to an increase in NO_2^- and NO_3^-.

Table 44: Chlorophyll, seston and nutrient concentrations determined for the samples taken in July 2004

samp. point	TCHL	Seston	RDP	DOP	TDP	NO_2^-	NO_3^-	NH_4^+	DIN	$Si(OH)_4$
	[µg L^{-1}]	[mg L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal1	26.7	47.9	4.60	-	-	1.01	6.47	53.20	60.68	26.03
Cal2	23.5	59.3	3.13	-	-	1.34	6.05	32.88	40.27	16.13
Cal3	19.3	49.4	5.07	-	-	1.61	6.50	70.72	78.83	60.59
Cal4	11.7	54.8	1.37	1.12	2.49	1.12	5.29	19.29	25.70	8.84
C5	33.1	86.7	0.93	1.56	2.49	0.78	3.65	15.63	20.07	7.48
C50	26.1	63.4	0.57	1.65	2.22	0.83	3.85	16.13	20.81	7.89
C350	19.5	64.7	0.77	0.65	1.42	0.82	3.53	16.47	20.82	7.97
C700	24.3	55.8	1.12	1.06	2.18	0.80	3.48	16.42	20.70	7.85
D5	6.3	42.6	0.33	0.93	1.26	0.12	2.42	3.73	6.27	2.34
D50	-	57.2	0.33	2.43	2.76	0.16	2.47	3.73	6.36	5.84
D350	-	46.9	0.35	0.80	1.16	0.05	1.92	4.10	6.08	2.29
D700	-	54.9	0.35	0.78	1.13	0.16	2.36	3.42	5.94	1.38
Dov2	-	55.1	0.33	0.73	1.06	0.12	2.38	4.63	7.13	3.62
Dov4	-	57.8	1.98	0.11	2.09	0.05	2.34	3.42	5.81	9.12
SD1	7.7	74.3	3.04	-	-	0.15	3.02	3.64	6.81	4.46
SD2	3.7	115.5	1.01	1.28	2.29	1.39	7.70	3.54	12.63	2.45
SCH1	2.1	51.4	1.83	0.35	2.18	0.04	1.33	2.88	4.25	3.82
SCH2	1.8	51.6	1.37	1.60	2.96	0.63	4.37	0.75	5.75	1.18
SCH3	2.5	145.9	1.28	1.10	2.38	0.03	17.25	5.55	22.83	9.48
SCH5	0.7	504.6	1.89	0.62	2.51	0.34	16.60	14.85	31.79	17.05
SCH6	1.7	73.2	0.42	0.70	1.12	0.33	16.83	8.60	25.75	5.34
SC1	14.7	59.8	0.35	2.41	2.76	0.42	2.79	7.20	10.42	3.60
SC2	12.4	56.7	0.33	1.82	2.15	2.99	4.05	7.17	14.21	5.19

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8.3.3 Polycyclic aromatic hydrocarbons

The PAH contents determined for the samples taken in Calais harbour on July 13th are shown in Table 70. Additionally the sum of the particulate and dissolved fraction is shown in Table 69. The highest total amount was observed at Point Cal 1 (Quai en eau profonde), the lowest was determined for the sample taken at the harbour entrance. Observed total amounts were between 46 ng L^{-1} and 69 ng L^{-1} and show only little variation. In all samples phenanthrene, fluoranthene and pyrene were the dominating compounds. High molecular weight PAHs were at almost all locations below the limit of detection.

The PAH contents determined for the samples taken in Dover are also shown in Table 70. The lowest contents were determined for the samples taken at Point D 5 and D50 and the highest contents were detected in the samples taken at point D 350 and point Dov 4. With exception of point D 350 almost no PAHs bound to particles were found and therefore no high molecular weight PAHs were present. The dominating component in all cases was phenanthrene. At some locations fluoranthene, pyrene and chrysene also were found .

The PAH contents determined for the samples taken from the seawater scrubber system are shown in Table 72. Comparing the inlet and outlet samples, the inlet samples always show very low contents. These were equally concentrated in Calais and the Channel and had lower contents in Dover. However the outlet samples show about 40 to 80 times higher total PAH contents than the inlet samples, but nevertheless 10 times lower than inside the system before the dilution with the cooling water. The total PAH amount behind the Ecosilencer and behind the US filter are nearly the same, whereas the sample behind the cyclone shows a lower content. The major differences are due to the phenanthrene, pyrene and fluoranthene contents.

Quality of measurement: Comparison 1st and 2nd extraction

Fig. 31 shows the results of the regression between the first and the second extraction. On the left the regression of the extracted material weight is shown. For this determination the filter which was used for the extraction of the particulate material was weighed before and after the extraction. Before the latter the filter was dried at 100 °C. The weight thus determined is not comparable to the total suspended material, because the filter was extracted and is therefore reduced in organic material, but it can be used to compare the amounts of extracted material between the first and the second extraction. On the right of Fig. 31 the regression of every single PAH compound of every single sample determined during the first extraction was plotted against those from the second extraction.

In both regressions the slope and the R^2 should be, in the best case, 1. This would show that for both cases the amount of extracted material was the same and that in both extractions the same PAH contents were measured. Due to the accuracy of the method (chapter 4.2) the R^2 and the slope might vary. As can be seen the difference is smaller than 4 % and therefore within the statistical range.

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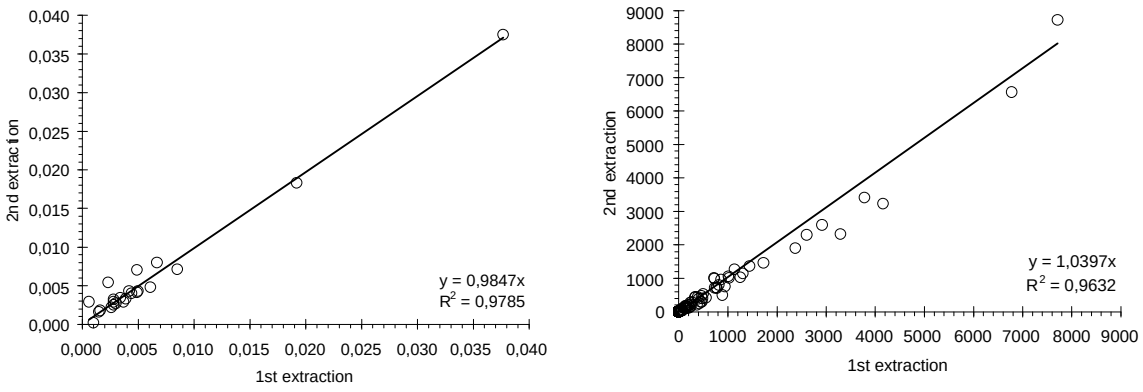

Fig. 31: Regression between 1st and 2nd extraction. Left: Regression of the amount of extracted particulate material [g]. Right: Regression of all PAHs [ng/L] (sum particulate, dissolved).

Origin of PAHs

In Fig. 32 the isomeric ratios of phenantrene/anthracene and fluoranthene/pyrene of the harbour samples and the seawater scrubber samples are shown. The Calais harbour samples show a behaviour similar to the harbour samples taken in February and March and are situated between a petrogenic and a pyrolytic origin. In contrast the samples taken in Dover seem to originate from a petrogenic pollution source.

Thehe Ecosilencer samples also show a comparable pattern. The PAHs from the sample behind the Ecosilencer and from those before and behind the US filter have high phenanthrene to anthracene ratios and low fluoranthene to pyrene ratios and are therefore most likely of petrogenic origin. The PAHs in the outlet samples seem to be of petrogenic origin but not as markedly as the undiluted samples. The inlet samples are comparable to the harbour samples.

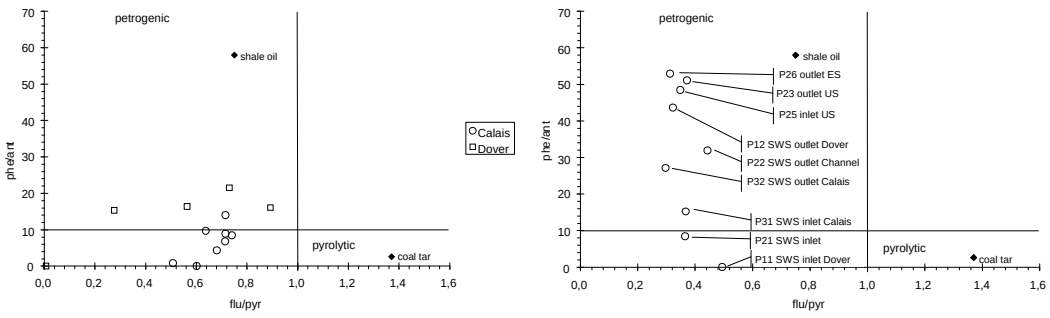

Fig. 32: Plot of isomeric phenanthrene/anthracene ratios against fluoranthene/pyrene ratios for all harbour samples (left) and seawater scrubber samples (right).

The ratios of benz[*a*]anthracene and chrysene, which can also be used to determine the origin of the PAHs in the samples are shown in Table 45. It can be seen that in most cases the contents of the two compounds were too low and therefore this index could not be used to determine the origin. Only the

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contents of the outlet and the seawater scrubber samples were high enough. The quotients of these samples are greater than one and therefore indicate pyrolytic origin.

Table 45: Quotient of benz[*a*]anthracene and chrysene.

sampl. point	Cal 1	Cal 2	Cal 3	Cal 4	C5	C50	C350	C700	
BaA/CHRY	1.00	0.00	-	-	1.00	-	-	-	
sampl. point	Dov 2	Dov 3	Dov 4	D5	D50	D350	D700		
BaA/CHRY	-	-	-	-	-	0.20	-		
sampl. point	SD1	SD2	SCH1	SCH2	SC1	SC2	SCH3	SCH5	SCH6
BaA/CHRY	0.00	1.89	0.00	1.47	0.00	1.86	2.63	2.46	2.26

Table 46: Regression of PAH components, yellow shows high correlation

	ATHY	ATHE	FLRE	PHEN	ANTH	FLUA	PYR	BaA	CHRY	BbkF	BaP	DahA	BghiP	INDE
ATHY	1	0.951	0.965	0.932	0.925	0.939	0.922	0.927	0.901	0.939	0.942	0.936	0.94	0.935
ATHE		1	0.979	0.98	0.957	0.982	0.967	0.972	0.943	0.984	0.992	0.978	0.986	0.983
FLRE			1	0.993	0.991	0.994	0.984	0.987	0.976	0.987	0.994	0.981	0.988	0.99
PHEN				1	0.99	0.999	0.996	0.998	0.99	0.991	0.993	0.979	0.988	0.976
ANTH					1	0.991	0.986	0.989	0.989	0.979	0.98	0.973	0.977	0.971
FLUA						1	0.994	0.998	0.988	0.993	0.994	0.982	0.99	0.98
PYR							1	0.995	0.994	0.977	0.981	0.959	0.972	0.959
BaA								1	0.992	0.991	0.989	0.979	0.987	0.97
CHRY									1	0.969	0.947	0.951	0.962	0.943
BbkF										1	0.996	0.996	0.999	0.986
BaP											1	0.99	0.997	0.993
DahA												1	0.998	0.988
BghiP													1	0.991
INDE														1

To examine whether the PAHs inside the harbour originate from one source the regression coefficients for the linear regression of the compounds were calculated. These calculations might show, whether the composition of the 16 EPA PAHs are comparable among each other. The results are shown in Table 46. It can be seen that all compounds are highly correlated. As many PAHs had values lower than the detection limit and some like phenanthrene appeared in high contents, the results might only “pretend” a high correlation. Therefore the R^2 was calculated for the linear regression of each station with the remaining stations. The results are shown in Table 47. It can be seen that sample Cal 3 does not correlate with any other sample, and that the samples taken from the seawater scrubber are only moderately correlated with the harbour samples. However the harbour samples and the inlet samples with exception of the Channel inlet sample also show a good correlation aa do the SWS samples among each other. In summary it can be said that the harbour samples and the seawater scrubber inlet samples show a similar PAH composition. The seawater

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scrubber samples make up another group which is not even comparable to the samples taken directly in front of the outlet of the “Pride of Kent”. The PAH composition of point Cal 3 is totally different from the remaining samples.

Table 47: Regression of sampling points. Colours are added for a better visualisation. Yellow - highly correlated, orange and red moderate or low correlation, dark red - no significant correlation.

	Cal 1	Cal 2	Cal 3	Cal 4	C05	C50	C350	C700	D05	D50	D350	D700	Dov 2	Dov 4	SD1	SD2	SCH1	SCH2	SCH3	SCH5	SCH6	SC1	SC2	
Cal 1	1	0.892	0.638	0.832	0.918	0.887	0.864	0.743	0.61	0.675	0.858	0.83	0.868	0.883	0.836	0.662	0.743	0.598	0.624	0.646	0.643	0.821	0.614	Cal 1
Cal 2		1	0.506	0.877	0.916	0.912	0.951	0.877	0.77	0.788	0.895	0.889	0.891	0.953	0.875	0.713	0.807	0.657	0.663	0.685	0.682	0.897	0.641	Cal 2
Cal 3			1	0.492	0.505	0.429	0.431	0.255	0.146	0.158	0.402	0.335	0.36	0.388	0.38	0.146	0.262	0.104	0.126	0.139	0.144	0.339	0.152	Cal 3
Cal 4				1	0.759	0.791	0.85	0.789	0.733	0.746	0.713	0.845	0.909	0.864	0.723	0.644	0.804	0.584	0.604	0.621	0.613	0.752	0.557	Cal 4
C05					1	0.89	0.881	0.789	0.672	0.722	0.892	0.824	0.836	0.911	0.836	0.707	0.708	0.646	0.671	0.689	0.687	0.844	0.654	C05
C50						1	0.952	0.932	0.829	0.864	0.858	0.964	0.906	0.957	0.948	0.75	0.825	0.69	0.702	0.728	0.716	0.924	0.659	C50
C350							1	0.95	0.836	0.872	0.821	0.959	0.921	0.957	0.891	0.738	0.843	0.682	0.692	0.715	0.702	0.899	0.644	C350
C700								1	0.934	0.946	0.779	0.975	0.91	0.93	0.888	0.793	0.866	0.752	0.751	0.772	0.752	0.893	0.677	C700
D05									1	0.976	0.702	0.908	0.832	0.856	0.8	0.821	0.843	0.775	0.778	0.796	0.779	0.852	0.693	D05
D50										1	0.738	0.94	0.88	0.892	0.834	0.851	0.883	0.811	0.807	0.825	0.808	0.882	0.723	D50
D350											1	0.812	0.807	0.863	0.913	0.799	0.81	0.764	0.753	0.773	0.776	0.931	0.764	D350
D700												1	0.949	0.947	0.926	0.802	0.912	0.754	0.757	0.78	0.762	0.924	0.694	D700
Dov 2													1	0.943	0.847	0.833	0.879	0.789	0.804	0.819	0.807	0.861	0.749	Dov 2
Dov 4														1	0.881	0.778	0.822	0.714	0.731	0.752	0.743	0.903	0.676	Dov 4
SD1															1	0.781	0.897	0.751	0.726	0.752	0.746	0.977	0.715	SD1
SD2																1	0.82	0.988	0.993	0.996	0.996	0.836	0.972	SD2
SCH1																	1	0.81	0.768	0.7889	0.78	0.924	0.738	SCH1
SCH2																		1	0.984	0.985	0.985	0.805	0.973	SCH2
SCH3																			1	0.999	0.997	0.78	0.978	SCH3
SCH5																				1	0.998	0.805	0.976	SCH5
SCH6																					1	0.803	0.986	SCH6
SC1																						1	0.769	SC1
SC2																							1	SC2

Principal component analysis

In Fig. 33 and in Table 48 the results of the PCA of all harbour samples and the SWS inlet samples taken in July are given. In this case eigenvector 1 accounts for 33.6 % and eigenvector 2 for19.7 % of the total variance. As both vectors only make up 52.3 % of the total variance only a part of the total variability within these samples can be explained. According to the PCA plot the samples can be divided into three groups. The first one is made up by C 50, C700, D 5, D 50, D 700, Dov 2, SD1 and SC1. These samples are all in the third quadrant meaning they are negative on both axes. Looking at the feature vector this indicates low overall concentrations and especially low anthracene, pyrene and fluoranthene concentrations. The second group is made up by the samples Cal 2, Cal 3, Cal 4, C 350 and Dov 4. These are in the second quadrant meaning they are positively related to eigenvector 2 and negatively related to eigenvector. As eigenvector 1 is mainly positive, this indicates, that the samples of this group have higher contents the more they are situated on the positive side. The third group is made up by Cal 1, C 5 and D 350. These samples also showed the highest overall concentration. The pattern that is drawn in Fig. 33 is nearly the same, which can be observed in the regression chart (Table 47). Cal 3, Cal 1, C5 and D350 are separated and have only low correlations with the remaining points, whereas the remaining points are higher correlated.

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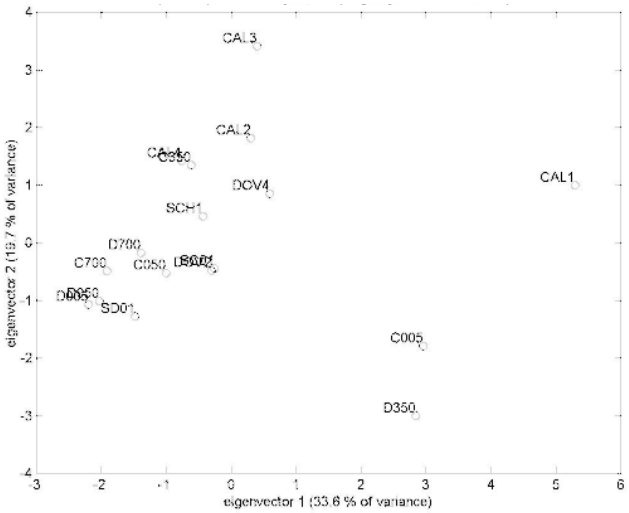

Fig. 33: Results of the PCA of the harbour samples

Table 48: Feature vector for the PCA of the harbour samples

	33.6 % (14.0)	19.7 % (14.0)
acenaphthylene	0.16	0.48
acenaphthene	-0.05	0.31
fluorene	-0.02	0.06
phenanthrene	0.23	-0.09
anthracene	0.15	0.50
fluoranthene	0.43	0.22
pyrene	0.41	0.27
benz[*a*]anthracene	0.38	-0.26
chrysene	0.18	-0.26
benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0.37	-0.09
benzo[*a*]pyrene	0.39	-0.11
dibenz[*a,h*]anthracene	0.27	-0.36
benzo[*ghi*]perylene	0.16	0.48
indeno(*1,2,3,c,d*)pyrene	-0.05	0.31

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8.4 4th sampling (September)

8.4.1 pH, salinity and temperature

The date and time when the samples were taken during the fourth sampling are given in Table 9. The high and low water times are shown in Table 8. It can be seen that in Calais the samples were taken during high tide and three hours after high tide. In Dover the samples were taken approximately one hour after ebb tide.

The pH, salinity, air and water temperatures are shown in Table 49 (Calais), Table 50 (Dover) and in Table 51 (seawater scrubber). The air temperatures during the sampling from the quay walls in Calais varied between 19.0 and 19.5 °C and the water temperature between 21.5 and 22.1 °C. During the sampling from the small boat at point C0, C5, C50, C350, C700 the air temperature was about 3 to 4 °C higher. The water temperature at point C5 and C50 was slightly increased (0.5 °C) whereas the remaining points had about the same water temperature as the samples taken from the harbour walls. The increase in temperature might be an effect of the seawater scrubber effluent.

Table 49: Temperature, salinity and pH data measured at the different sampling points in Calais harbour in September

Point	Temp [°C] air	Temp [°C] water	Sal [PSU]	pH
Cal 1	19.5	22.1	34.1	7.95
Cal 2	19.5	22.1	34.0	7.97
Cal 3	19.0	21.5	31.9	7.89
Cal 4	19.1	21.9	33.7	8.04
C 0	22.3	23.3	34.3	8.08
C 5	23.5	23.1	34.6	8.08
C 50	23.0	22.8	34.7	8.09
C 350	22.2	22.8	34.7	8.09
C 700	22.2	22.9	34.6	8.10

Table 50: Temperature, salinity and pH data measured at the different sampling points in Dover harbour in September

Point	Temp [°C] air	Temp [°C] water	Sal [PSU]	pH
D 5	26.9	22.8	35.1	8.07
D 50	24.4	22.3	35.2	8.04
D 350	25.1	22.1	35.0	8.05
D 700	23.6	22.1	35.0	8.04
Dov 1	23.3	22.2	35.0	8.07
Dov 2	22.6	22.2	35.1	8.08
Dov 3	22.6	21.9	35.1	8.08
Dov 4	25.0	22.2	35.2	8.08

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Table 31 shows that the seawater scrubber outlet water was 13 to 17 °C warmer than the inlet water. This difference is more than 10 °C higher than those observed during the first three samples. An increased temperature was also observed at the first and second points in Dover in a distance of 5 and 50 m away from the outlet. At point D 5 the temperature was 0.7 °C higher than at the remaining points inside the harbour, with the exception of point Dov 3 in the middle of the port, where the temperature was the lowest (21.9 °C). Inside the seawater scrubber system the highest temperatures were measured directly after the Ecosilencer, in front of and behind the US-filter. Here the temperatures were 45.1, 45.3 and 46.2 °C, respectively. The water in the seawater scrubber outlet still had a temperature of 35.7, 37.1 and 37.6 °C. The pH inside the harbour was nearly constant for all samples with exception of the samples taken from the quay walls in Calais. Inside the seawater scrubber system the lowest pH (3.05) was determined in the pipe leading to the settling tank and also behind the US filter. The outlet water in Dover, the Channel and Calais showed a pH of 6.2, 6.4 and 6.15, respectively. It was about 1.7 pH units lower in comparison to the inlet water. The samples taken inside the Channel had a salinity of about 37 whereas in Calais and Dover the salinity varied between 34 and 35. At point Cal 3 a salinity of only 31.9 was observed due to the enclosed situation of that sampling point.

Table 51: Temperature, salinity and pH data measured at the different sampling points in the seawater scrubber in September

Point	Temp [°C] water	Sal [PSU]	pH
SD1	24.0	34.4	7.99
SD2	37.6	35.7	6.20
SCH1	23.0	36.0	8.08
SCH2	37.1	36.0	6.40
SCH3	45.3	36.8	3.14
SCH4	42.5	36.6	3.05
SCH5	46.2	36.8	3.05
SCH6	45.1	36.4	3.13
SCH7	38.5	37.0	3.04
SC1	20.7	34.5	7.88
SC2	37.6	34.7	6.15

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8.4.2 Nutrients

The chlorophyll, seston and nutrient concentrations determined for the samples taken in September are shown in Table 52. It can be seen that in Dover the chlorophyll concentration was generally lower than in Calais. The highest chlorophyll content was measured at point Cal 3 (181.9 µg L^{-1}). At this point also the highest seston, silicate, ammonium and RDP concentrations ws determined, whereas the nitrate concentration was the lowest observed in all samples. This shows that there was an algal bloom at this point. The nitrate concentration was reduced because it is used as an important nitrogen supply. Ammonium is the first degradation product of nitrogen-containing organic material. Hence the higher concentrations in the harbour waters of Calais indicate that somde degradation already had taken place. At the remaining points in Calais the chlorophyll concentrations varied between 5.1 and 48.4 µg L^{-1}. The lowest value was observed at point Cal 1 and the highest at C350. In Dover Chlorophyll concentration between 4.2 (Dov 4) and 12.8 µg L^{-1} (D350) were observed. The RDP, DOP, TDP, seston and silicate values were all within the same range as in Calais, whereas the nitrate concentrations were increased and the ammonium concentrations were lower in Dover. Taking a look at the first transect samples D5 and C5 it can be seen that the nitrate concentrations are slightly increased in comparison to the other points. This could be an effect of the seawater scrubber but also of eutrophication due to the enclosed area and the ship traffic.

Table 52: Chlorophyll, seston and nutrient concentrations determined for the samples taken in September 2004

samp. point	TCHL	Seston	RDP	DOP	TDP	NO_3^-	NH_4^+	DIN	$Si(OH)_4$
	[µg L^{-1}]	[mg L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal1	5.1	54.8	0.87	0.13	1.00	4.05	12.60	17.29	7.82
Cal2	16.2	56.7	0.97	0.07	1.04	3.76	14.20	18.60	8.57
Cal3	181.9	100.8	4.50	0.31	4.81	0.75	41.93	43.19	14.73
Cal4	22.9	64.0	0.65	0.31	0.96	3.52	9.28	13.36	6.92
C0	23.2	86.0	0.47	0.52	0.99	2.79	8.28	11.59	6.83
C5	35.3	76.2	0.39	0.61	0.99	3.58	9.95	14.02	6.84
C50	43.2	89.2	0.37	0.56	0.94	2.78	7.93	11.19	6.64
C350	48.4	76.5	0.37	0.19	0.56	2.52	9.02	12.02	5.04
C700	44.9	67.3	0.23	0.50	0.73	2.86	8.14	11.47	4.15
D5	7.2	59.5	0.55	0.35	0.90	2.86	0.63	3.80	6.78
D50	10.5	59.7	0.65	0.06	0.70	2.50	1.50	4.31	6.46
D350	12.8	58.8	0.23	0.24	0.47	2.58	1.44	4.31	4.94
D700	10.0	72.6	0.19	0.13	0.32	4.33	0.34	5.06	5.00
Dov1	5.9	74.8	0.55	0.23	0.78	7.37	1.22	9.07	6.02
Dov2	9.9	61.3	0.44	0.09	0.53	5.43	1.38	7.29	5.00
Dov3	7.6	65.6	0.44	0.08	0.52	5.32	1.41	7.19	6.49
Dov4	4.2	66.0	0.21	0.03	0.24	4.27	1.78	6.35	6.02
SD1	16.5	62.1	0.23	0.09	0.32	3.63	1.43	5.39	6.81
SD2	9.6	69.9	0.22	0.08	0.30	7.66	2.42	10.79	6.00
SCH1	5.7	57.8	0.20	0.09	0.29	3.96	2.26	6.63	3.89
SCH2	6.1	55.0	0.20	0.03	0.23	3.77	2.08	6.27	3.15
SCH3	10.2	54.1	0.78	0.29	1.07	19.21	4.33	23.61	7.58
SCH4	9.6	70.6	1.35	0.23	1.59	21.58	8.40	30.61	12.31
SCH5	6.7	61.1	0.83	0.10	0.93	18.27	3.67	22.01	6.95
SCH6	4.6	57.6	0.99	0.09	1.08	17.85	3.40	21.32	10.04
SCH7	7.4	99.1	1.54	0.08	1.62	21.05	4.90	26.10	12.28
SC1	49.1	61.8	0.64	0.15	0.79	3.76	8.33	12.63	8.70
SC2	32.0	64.2	0.42	0.23	0.65	5.52	7.37	13.54	7.60

Looking at the seawater scrubber inlet and outlet samples it can be seen that the nitrate concentrations are higher in the outlet, in Calais they even doubled. On board, the highest nitrate concentrations were not observed directly behind the Ecosilencer but at point SCH4, the pipe leading

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to the settling tank, and at point SCH7, the settling tank. These points also show high TDP, silicate and seston values. As silicate is the main substance of which diatom tests are built up it is not surprising that it is enriched by the cyclones in the seawater scrubber system. Comparing the inlet and outlet samples it can be seen that the nitrate concentration due to the formation of nitric acid in the Ecosilencer is increased. Additionally the seston content is higher in the outlet samples. This might result from remaining soot particles originating from the scrubbing process.

8.4.3 Metals and Sulphate

Table 53 shows the sulphate, earth and transition metal concentrations determined for the samples taken in Dover and Calais directly in front of the seawater scrubber outlet and inside the seawater scrubber system. It can be seen that As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb could not be detected. Fe was only found inside the seawater scrubber system but not in the inlet and the outlet. The highest iron content (4513 ppb) was found at point SCH4 in the pipe leading to the settling tank. One reason is the very low pH measured at this point which increases the solubility of iron. Another reason is that all particles collected in the seawater scrubber system, which also contain rust, are concentrated in the cyclones and pass this pipe, and a third aspect might be an overflow pipe from the funnel which flows into the settling tank pipe shortly before point SCH4 and which might contain particles and rust from the funnel. The same reasons might be responsible for the high vanadium concentration measured at point SCH4. However K, Li and Mg have nearly constantly contents in all samples, whereas the strontium concentration is higher in Calais than in Dover.

Table 53: Sulphate, earth and transition metals determined for the samples taken in September (- below detection limit)

		SD 1	SD2	SCH1	SCH2	SCH3	SCH4	SCH5	SCH6	SC2	SC 1
As	ppb	-	-	-	-	-	-	-	-	-	-
Ba	ppb	-	-	-	-	-	-	-	-	-	-
Ca	ppm	393	397	383	386	404	407	404	411	411	389
Cd	ppb	-	-	-	-	-	-	-	-	-	-
Co	ppb	-	-	-	-	-	-	-	-	-	-
Cr	ppb	-	-	-	-	-	-	-	-	-	-
Cu	ppb	-	-	-	-	-	-	-	-	-	-
Fe	ppb	-	-	-	-	803	4513	687	680	-	-
K	ppm	380	380	390	340	360	400	400	380	370	330
Li	ppb	180	180	170	180	180	180	180	180	180	180
Mg	ppm	1235	1230	1205	1205	1260	1265	1255	1290	1265	1220
Mn	ppb	-	-	-	-	-	-	-	-	-	-
Mo	ppb	-	-	-	-	-	-	-	-	-	-
Ni	ppb	-	-	-	-	-	-	-	-	-	-
Pb	ppb	-	-	-	-	-	-	-	-	-	-
SO4	ppm	2670	2710	2590	2600	2940	2940	2990	2980	2870	2590
Sr	ppb	7680	7760	7515	7705	7915	7915	8020	8055	8035	7620
V	ppb	-	-	-	-	155	420	240	170	-	-
Zn	ppb	-	290	-	-	455	-	395	360	-	-

Zinc was only determined in the outlet sample in Dover and at points SCH3, SCH5 and SCH6, but not in the pipe going to the settling tank and in no other outlet sample. The source for this contamination

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might be the valves used during the sampling which might contain zinc. Otherwise if zinc would originate from the system itself it should also have been detected at point SCH4 and in the outlet water.

As expected the sulphate concentration was increased inside the seawater scrubber due to the formation of sulphuric acid, but comparing the in and outlet sample taken in the Channel no increase was observed.

Summarising the data of Table 53 it can be said that no increase in the metal or sulphate concentration was observed outside the “Pride of Kent” and that the increased Fe and V concentrations were only observed inside the pipe leading to the settling tank. As the water and the particles from the settling tank will be treated in a special way (deposition or burning), and as Fe and V are not toxic, no negative effect is to be expected.

8.4.4 Polycyclic aromatic hydrocarbons

The concentrations of the determined dissolved and particle bound PAHs are shown in Table 70 and Table 72.The total amounts of all EPA PAHs (without naphthalene) are given in Table 69. Comparing the total amounts with the samplings in February, March and July, it can be seen that the contents in September were especially in Calais about 100 ng L^{-1} higher than in July, but the overall concentrations where not as high as in March or February. All analysed concentrations were situated between 44 and 248 ng L^{-1} with exception of the outlet samples where concentrations of 3422, 3263 and 3577 ng L^{-1} were determined. Taking a closer view at the single compounds it can be seen that almost no acenaphthene, acenaphthylene, anthracene, benzo[*b*+*k*]fluoranthene, benz[*a*]pyrene, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene or indeno[1,2,3,c,d]pyrene were present. In all samples phenanthrene, fluoranthene and pyrene dominated. These three compounds as well as fluorene were also the dominating compounds in the seawater scrubber effluent, where phenanthrene concentrations of 1400 ng L^{-1} were detected. No increased contents of high molecular weight PAHs were found in the outlet samples.

Looking at the PAH concentration determined 5, 50, 350 and 700 m away from the seawater scrubber outlet no increase was observed. In contrary the transect samples taken in Calais show lower PAH concentrations than the samples taken from the quay walls. Additionally the blank sample taken before the “Pride of Kent” arrived showed a higher PAH concentration (133 ng L^{-1}) than the sample taken at point C 5 (109 ng L^{-1}). In Dover the sample taken 5 m away from the outlet had a content similar to the sample from the middle port at point Dov 2. All these observations show that the seawater scrubber effluent does not seem to increase the PAH concentration.

Inside the seawater scrubber all four- and five-ring compounds with the exception of fluoranthene and pyrene were nearly completely found bound to the particulate fraction. Phenanthrene which partially made up about 50 % of the total amount of all measured PAHs was also found in high concentrations

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in the particulate fraction. This shows that most of the PAHs are bound to soot particles, and that an effective remove of these particles is able to lower these concentrations significantly.

Quality of measurement: Comparison 1st and 2nd extraction

Fig. 34 shows the regression of the extracted and dried filters and of the determined PAHs (chapter 8.3.3). In both cases high correlation coefficients and slopes close to one were observed. Therefore the results of the first and the second extraction are very similar.

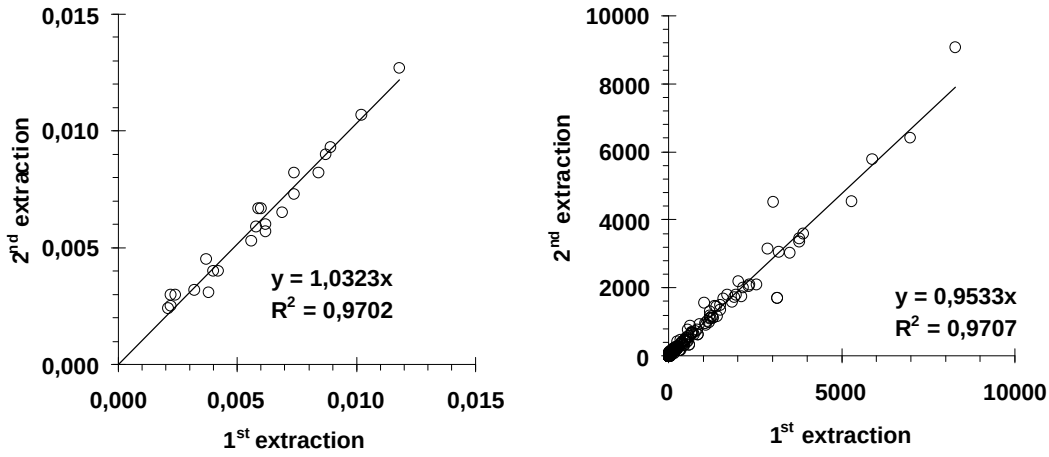

Fig. 34: Regression between 1st and 2nd extraction left: Regression between the amount of extracted particulate material [g]. Right: Regression of all determined PAH concentrations [ng/l] (sum, particulate, dissolved).

Origin of PAHS

To determine the origin of the PAHs a regression of the compound concentrations among each other and a regression of the concentrations determined at the single sampling points was performed. The results are shown in Table 55 and Table 54.

The correlation coefficients of Table 54 show high correlation coefficients for nearly all compounds. When a high correlation between for example fluoranthene and pyrene was found this meant that at all points where high concentrations of fluoranthene were measured, also high concentrations of phenanthrene were measured. If the relative relations of all compounds were the same at all points, and differences only appear in the concentration itself, high correlation coefficients would be observed for all compounds. As the anthracene concentrations were often close to or lower than the detection limit, the R^2 for the correlation with this compound is low. The same reason can be given for the low R^2 observed for the correlations with dibenz[*ah*]anthracene and acenaphthylene. As this method of regression analysis is not very specific and gives no information about the similarity of single sampling points, a regression of the observed PAH concentrations of the sampling points was also performed.

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Table 54: Regression of compounds. Colours are added for a better visualisation. Yellow - highly correlated, dark red - no significant correlation.

	ATHY	ATHE	FLRE	PHEN	ANTH	FLUA	PYR	BaA	CHRY	BbkF	BaP	DahA	BghiP	INDE
ATHY	1	0.787	0.819	0.851	0.619	0.876	0.874	0.851	0.891	0.93	0.759	0.921	0.941	0.934
ATHE		1	0.994	0.988	0.927	0.976	0.978	0.974	0.966	0.7	0.948	0.824	0.753	0.815
FLRE			1	0.997	0.918	0.99	0.991	0.987	0.982	0.74	0.959	0.851	0.79	0.843
PHEN				1	0.895	0.996	0.998	0.991	0.992	0.778	0.952	0.878	0.823	0.872
ANTH					1	0.872	0.873	0.9	0.855	0.487	0.952	0.608	0.548	0.601
FLUA						1	0.999	0.989	0.996	0.815	0.942	0.899	0.856	0.896
PYR							1	0.991	0.997	0.811	0.943	0.898	0.852	0.894
BaA								1	0.993	0.769	0.974	0.848	0.805	0.843
CHRY									1	0.831	0.943	0.902	0.863	0.899
BbkF										1	0.645	0.956	0.99	0.965
BaP											1	0.728	0.689	0.722
DahA												1	0.97	0.997
BghiP													1	0.981
INDE														1

Table 55: Regression of sampling points. Colours are added for a better visualisation. Yellow highly correlated, orange and red moderate or low correlation, dark red no significant correlation.

	Cal1	Cal2	Cal3	Cal4	C0	C5	C50	C350	C700	D5	D50	D350	D700	Dov2	Dov3	Dov4	SD1	SD2	SCH1	SCH2	SCH3	SCH4	SCH5	SCH6	SC1	SC2	
Cal1	1	0,926	0,837	0,835	0,914	0,957	0,893	0,942	0,935	0,791	0,918	0,675	0,628	0,982	0,801	0,715	0,929	0,785	0,769	0,743	0,761	0,731	0,752	0,771	0,811	0,768	Cal1
Cal2		1	0,745	0,824	0,878	0,940	0,839	0,934	0,859	0,782	0,840	0,575	0,502	0,893	0,753	0,599	0,827	0,754	0,683	0,701	0,733	0,738	0,727	0,731	0,727	0,740	Cal2
Cal3			1	0,852	0,889	0,815	0,936	0,758	0,781	0,877	0,896	0,865	0,843	0,830	0,881	0,931	0,886	0,893	0,931	0,882	0,882	0,837	0,868	0,898	0,917	0,884	Cal3
Cal4				1	0,968	0,817	0,958	0,757	0,778	0,977	0,795	0,866	0,769	0,802	0,975	0,822	0,896	0,947	0,908	0,919	0,941	0,930	0,945	0,936	0,950	0,943	Cal4
C0					1	0,904	0,974	0,856	0,879	0,932	0,855	0,818	0,740	0,872	0,946	0,816	0,915	0,900	0,877	0,865	0,882	0,858	0,880	0,889	0,930	0,892	C0
C5						1	0,858	0,972	0,945	0,775	0,914	0,616	0,585	0,905	0,770	0,650	0,834	0,765	0,735	0,719	0,737	0,712	0,730	0,749	0,779	0,745	C5
C50							1	0,811	0,877	0,948	0,879	0,886	0,810	0,882	0,971	0,900	0,943	0,938	0,935	0,913	0,917	0,882	0,924	0,931	0,958	0,930	C50
C350								1	0,917	0,690	0,895	0,520	0,472	0,896	0,697	0,568	0,785	0,675	0,657	0,619	0,645	0,621	0,631	0,654	0,690	0,649	C350
C700									1	0,753	0,943	0,679	0,683	0,909	0,783	0,746	0,841	0,766	0,775	0,734	0,743	0,705	0,729	0,758	0,804	0,747	C700
D5										1	0,784	0,919	0,929	0,770	0,978	0,878	0,889	0,982	0,944	0,970	0,977	0,964	0,985	0,978	0,970	0,986	D5
D50											1	0,711	0,708	0,917	0,795	0,768	0,868	0,827	0,843	0,797	0,801	0,752	0,777	0,819	0,823	0,800	D50
D350												1	0,962	0,681	0,939	0,970	0,844	0,937	0,963	0,955	0,936	0,893	0,946	0,949	0,963	0,945	D350
D700													1	0,638	0,861	0,947	0,782	0,886	0,925	0,917	0,891	0,841	0,890	0,905	0,917	0,892	D700
Dov2														1	0,786	0,733	0,949	0,782	0,768	0,745	0,755	0,721	0,747	0,770	0,793	0,765	Dov2
Dov3															1	0,903	0,901	0,966	0,953	0,953	0,953	0,923	0,968	0,963	0,983	0,965	Dov3
Dov4																1	0,861	0,904	0,953	0,919	0,897	0,847	0,901	0,919	0,937	0,908	Dov4
SD1																	1	0,896	0,884	0,874	0,877	0,841	0,879	0,891	0,910	0,890	SD1
SD2																		1	0,972	0,995	0,991	0,965	0,995	0,999	0,973	0,998	SD2
SCH1																			1	0,974	0,963	0,913	0,959	0,978	0,979	0,966	SCH1
SCH2																				1	0,990	0,962	0,994	0,998	0,969	0,996	SCH2
SCH3																					1	0,988	0,990	0,992	0,966	0,992	SCH3
SCH4																						1	0,971	0,964	0,928	0,970	SCH4
SCH5																							1	0,995	0,970	0,999	SCH5
SCH6																								1	0,976	0,998	SCH6
SC1																									1	0,972	SC1
SC2																										1	SC2

Taking Table 55 into closer view, it can be seen that most of the sampling points are highly correlated. Especially the correlation between the seawater scrubber samples among each other and the Calais samples among each other showed high R^2 values indicating that the PAH composition of these samples is similar. In contrary the correlation of the samples taken from the harbour in Dover seem to be different in their composition from the samples taken in Calais. They show only moderate correlation coefficients for these regressions, but high correlation coefficients when compared with the seawater scrubber samples. The samples taken from the Calais transect are only moderately correlated with the samples taken from the seawater scrubber. Summarising can be said, that all Dover samples show a comparable composition while the Calais samples are not comparable to the seawater scrubber samples. Therefore the composition of the Dover and Calais samples is different too.

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Additionally to the regression analysis a principal component analysis (Fig. 36, Table 57) and an analysis of the isomeric ratios of phenanthrene to anthracene, fluoranthene to pyrene (Fig. 35) and benz[*a*]anthracene to chrysene (Table 55) was performed. The plot of the phen/anth ratios against the flua/pyr ratios indicates that the seawater scrubber samples seem to originate from a petrogenic source. This would underline the results of the previous samplings. The same holds for the isomeric ratios of benz[*a*]anthracene and chrysene which are all smaller than one and therefore indicate a pyrolytic origin too.

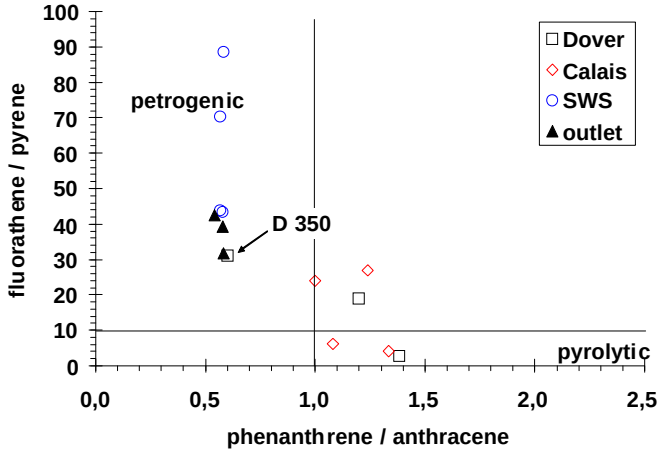

Fig. 35: Plot of isomeric phenanthrene/anthracene ratios against fluoranthene/pyrene ratios for all samples

The phenanthrene to anthracene ratios of the harbour samples are close to ten and the fluoranthene to pyrene and the benz[*a*]anthracene to chrysene ratios are close to one. This might have the same reasons as those mentioned in the discussion of the February, March and July samplings. The explicit petrogenic character of the sample D 350, which shows nearly the same isomeric ratios as the outlet samples cannot be explained. Perhaps a thin oil film flowing on top of the water contaminated this sample.

The principal component analysis underlines and specifies the results of the regression analysis. From this the samples can be divided into three different groups. The first group is made up by only one sample: Cal 2. This sample is characterised by relative high anthracene, fluoranthene and pyrene contents. As point Cal 2 is situated close to the place where the service boats anchor, these might originate from the lighter petroleum used for these boats.

Table 56: The quotient of benz[*a*]anthracene to chrysene can be used as marker for the origin of a sample

sampl. point	Cal 1	Cal 2	Cal 3	Cal 4	C0	C5	C50	C350	C700	
BaA/CHRY	0,2	0,9	0,8	0,6	0,6	0,0	1,2	1,0	1,0	
sampl. point	Dov 2	Dov 3	Dov 4	D0	D5	D50	D350	D700		
BaA/CHRY	0,7	0,8	1,0		0,6		0,7	0,4		
sampl. point	SD1	SD2	SCH1	SCH2	SC1	SC2	SCH3	SCH4	SCH5	SCH6
BaA/CHRY	0,6	0,6	0,6	0,5	0,5	0,5	0,5	0,5	0,6	0,5

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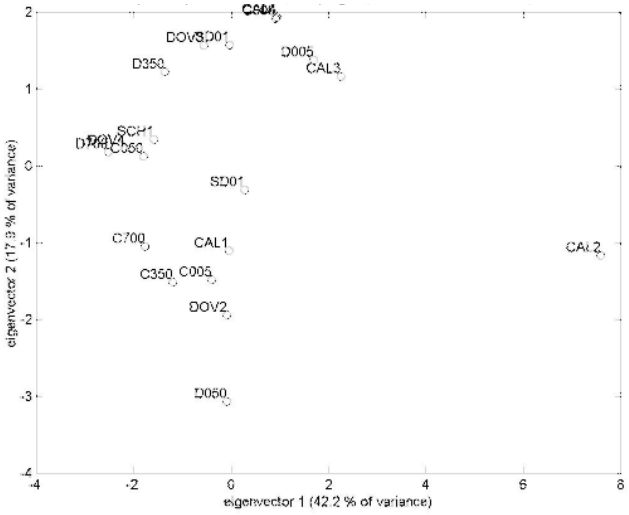

Fig. 36: Results of the PCA of the harbour samples

Table 57: Feature vector for the PCA of the harbour samples

	42.2 % (14.0)	17.9 % (14.0)
acenaphthylene	0.14	0.20
acenaphthene	0.28	0.19
fluorene	0.13	0.18
phenanthrene	0.30	-0.08
anthracene	0.15	-0.34
fluoranthene	0.32	-0.41
pyrene	0.39	-0.22
benz[*a*]anthracene	0.24	0.51
chrysene	0.20	0.52
benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0.40	0.02
benzo[*a*]pyrene	0.36	-0.12
dibenz[*a,h*]anthracene		
benzo[*ghi*]perylene	0.36	-0.03
indeno(*1,2,3,c,d*)pyrene	0.14	0.20

The second group is made up by the samples D 50, Dov 2, C 350, C 5, Cal 1, C 700 and SD1. For these samples both eigenvectors are negative. The second eigenvector which is plotted on the y-axis mainly shows high chrysene, benz[a]anthracene and indeno(1,2,3,*c,d*)pyrene concentrations. All the samples of this group were taken close to the entrances of the ports of Dover and Calais. These points were influenced from the channel water which was not influenced by port activities and therefore contained less petroleum-derived PAHs.

The third group is made up from the samples inside the harbour and it makes no difference whether they were taken from the transect or not. Therefore it can be stated, that the samples are quite similar within their composition and that the seawater scrubber obviously does not change this composition significantly.

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8.5 5th sampling (November)

8.5.1 pH, salinity and temperature

The sampling dates as well as the high and low water times are shown in Table 8 and Table 9. The samples in Calais were taken during low tide and the samples in Dover during high tide.

The air and water temperatures, the pH and the salinity determined for the samples taken in Calais, Dover and inside the “Pride of Kent” are shown in Table 58,Table 59 and Table 60. The air temperature in Calais was 13 °C at all points. The water temperature was a little bit lower and varied between 11.1 and 11.6 °C. A temperature increase in front of the outlet of the seawater scrubber at point C 5 as it was observed during the sampling in July and September could not be detected this time.

As mentioned before, the samples from point C0 and C5 were not taken from the same position. C0 was taken before the arrival of the “Pride of Kent” but at a parallel quay farer inside the port. That is why the pH was lower than at point C5 and closer related to the pH observed at point Cal 2. The lowest pH was measured, comparable to the sampling before, at point Cal 3. This point also showed a lower salinity (30.7) than the remaining points. The reason might be the enclosed position of this point. The floodgate which can be seen in the map in Table 6 is only opened twice a day and therefore there is only little water exchange and the water is getting more brackish at the surface and stratification is enforced. At the remaining points the salinity was nearly constant and varied between 32.8 and 33.0 with exception of point Cal 2 where a salinity of only 23.5 was observed.

In Dover the pH range was smaller than in Calais. The lowest pH (8.15) was observed at point Dov 3 and the highest (8.26) at point D50. Within the transect samples no significant decrease or increase in pH was observed. The water and the air temperature was nearly constant at all points and also the salinity varied only between 34.2 and 34.3

Table 58: Temperature, salinity and pH data measured at the different sampling points in Calais harbour in November 2004

Point	Temp [°C] air	Temp [°C] water	pH	Sal [PSU]
Cal 1	13.0	11.6	7.95	32.5
Cal 2	13.0	11.4	7.76	23.5
Cal 3	13.0	11.1	7.92	30.7
Cal 4	13.0	11.5	8.18	32.9
C 0	13.0	11.5	7.86	32.9
C 5	13.0	11.6	8.12	32.8
C 50	13.0	11.6	8.11	32.8
C 350	13.0	11.6	8.12	32.8
C 750	13.0	11.5	8.12	33.0

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Table 59: Temperature, salinity and pH data measured at the different sampling points in Dover harbour in November 2004

Point	Temp [°C] air	Temp [°C] water	pH	Sal [PSU]
D 0	13.0	11.7	8.23	34.2
D 5	13.0	11.6	8.24	34.2
D 50	13.0	11.6	8.26	34.3
D 350	13.0	11.7	8.25	34.3
D 750	13.0	11.6	8.17	34.3
Dov 1	13.0	11.6	8.21	34.4
Dov 2	13.0	11.6	8.18	34.4
Dov 3	13.0	11.5	8.15	34.3
Dov 4	13.0	11.5	8.19	34.3

Table 60: Temperature, salinity and pH data measured at the different sampling points in the seawater scrubber harbour in November 2004

Point	Temp [°C] water	pH	Sal [PSU]
SD1	13.2	8.32	33.9
SD2	27.4	6.47	34.8
SCH1	14.0	8.28	34.3
SCH2	26.2	6.66	35.0
SCH3	35.5	3.35	35.7
SCH4	34.1	2.67	35.9
SCH5	35.4	3.34	35.6
SCH6	36.9	3.30	35.8
SCH8	24.1	3.79	35.0
SC1	13.6	7.81	33.0
SC2	25.5	6.33	33.5

Inside the seawater scrubber system the water temperature was highly variable. The lowest temperatures (13.2, 14.0 and 13.6 °C) were measured in the inlet samples. In the outlet the temperature was about 12 to 14 °C higher. The highest temperature was measured at point SCH6 (36.9 °C) directly behind the seawater scrubber. It slightly decreased at points SCH3 and SCH5 to 35.5 °C. The salinity inside the channel was slightly higher than inside the ports of Dover and Calais. The pH values in the inlet were 8.32 in Dover, 8.28 in the Channel and 7.81 in Calais. These values are comparable to the values measured outside the “Pride of Kent”. The lowest pH was measured at point SCH4. An explanation might be an overflow valve from the funnel reaching the pipe shortly before the sampling point. The pH values at points SCH6, SCH5 and SCH3 were nearly constant with 3.30, 3.34 and 3.35. The outflowing water showed a pH between 6.33 and 6.66. It can be seen that the dilution with cooling water increased the pH and directly in front of the outlet no decrease in pH was measured.

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8.5.2 Metals and Sulphate

The sulphate, earth and transition metal contents are shown in Table 61. It can be seen that chromium, manganese and molybdenum could only be determined in the settling tank and in the pipe leading to the settling tank. The reason for this might be, as explained before, the low pH and the concentration of particles in the cyclones and the settling tank.

Copper was measured at all points with the exception of point SCH1. An increase of the copper content due to the seawater scrubber cannot be stated for sure especially as during the sampling in September no copper could be determined. During the sampling in March high copper concentrations were also detected inside the settling tank. With respect to the inlet and outlet samples, copper is even decreasing in Calais.

The iron contents were again highest inside the settling tank. Here values up to 70 times higher than those at the remaining seawater scrubber points were observed. In the outlet water only in Dover an increased iron content was measured. Molybdenum, vanadium and nickel, also contents of ship steel, were found especially in the seawater scrubber system. Tin concentrations varied in the system but were higher in the outlet samples in comparison to the inlet samples. At point SCH4 no tin was found and inside the settling tank no increased tin content was observed. This again shows that the determined tin most probably originates from the sampling procedure. Potassium, lithium and magnesium had equal contents in all samples. These earth metals are conservative due to their reactivity and their concentration only depends on salinity.

Table 61: Sulphate, earth and transition metals determined for the samples taken in November 2004

		SC1	SC2	C 5	SCH1	SCH2	SCH3	SCH4	SCH5	SCH6	SCH8	SD1	SD2	D 5
Ca	ppm	397	402	384	368	400	400	407	406	406	405	385	388	388
Cr	ppb	-	-	-	-	-	-	74	-	-	362	-	-	-
Cu	ppb	119	48	35		32	74	40	60	100	1138	37	48	46
Fe	ppb	-	-	74	-	-	750	5292	481	585	33479	62	93	79
K	ppm	388	392	353	352	386	382	386	378	381	379	359	355	361
Li	ppm	178	180	163	168	184	181	183	184	183	183	170	170	167
Mg	ppm	1238	1251	1186	1157	1256	1255	1272	1263	1270	1251	1198	1185	1239
Mn	ppb	-	-	-	-	-	-	-	-	-	148	-	-	-
Mo	ppb	-	-	-	-	-	-	-	-	-	13	-	-	12
Ni	ppb	-	34	-	-	-	68	150	59	64	583	-	-	-
Pb	ppb	31	24	-	-	18	-	-	-	-	-	-	34	-
SO4	ppm	2699	2864	2578	2685	2805	3008	3140	3055	3061	3038	2587	2644	2669
Sr	ppm	8008	8054	7489	7693	8278	8087	8118	8264	8183	8203	7821	7731	7496
V	ppb	-	-	-	-	-	197	304	201	208	2676	-	29	-
Zn	ppb	-	229	-	-	96	426	-	266	454	465	31	147	-

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8.5.3 Nutrients

The seston and nutrient concentrations determined for the samples taken in November 2004 are shown in Table 62. In Calais the mean seston contents were about 100 mg L^{-1} higher than those observed in Dover. The highest concentrations were observed at points Cal 3 and Cal 4. The lowest were determined for point Dov 3. Inside the seawater scrubber system a significant increase was only measured at point SCH8. Comparing the inlet and outlet it can be seen that the concentrations in the inlet samples are comparable to those measured inside the harbours. In Dover the outlet water contained more suspended material than the inlet water. In Calais and in the Channel it was the reverse case. In Calais the concentration was even the half the concentration of the inlet sample.

Table 62: Seston and nutrient concentrations determined for the samples taken in November 2004

samp. point	Seston	RDP	DOP	TDP	NO_2^-	NO_3^-	NH_4^+	DIN	$Si(OH)_4$
	[mg L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]	[µmol L^{-1}]
Cal1	148.9	0.70	4.89	5.59	0.82	14.51	10.72	26.05	22.23
Cal2	122.1	12.97	2.25	10.73	3.32	44.86	27.10	75.27	124.14
Cal3	181.1	1.21	0.66	1.87	2.29	26.71	14.75	43.75	32.22
Cal4	184.9	0.59	2.75	3.35	0.89	14.41	9.48	24.78	20.81
C0	101.6	0.86	5.81	6.67	0.76	12.26	9.79	22.81	18.16
C5	93.1	0.15	1.52	1.67	1.50	17.15	50.27	68.92	22.28
C50	131.5	0.51	3.35	3.85	0.96	13.43	10.55	24.95	18.18
C350	126.3	0.59	2.07	2.67	0.87	13.35	10.68	24.90	18.18
C700	63.7	0.57	5.09	5.66	0.72	11.67	9.64	22.03	15.55
D0	25.4	0.64	6.32	6.96	1.09	16.46	1.56	19.10	6.99
D5	26.9	0.68	6.17	6.85	1.14	16.47	1.56	19.16	7.14
D50	70.3	0.70	3.72	4.43	1.10	16.40	1.62	19.12	5.95
D350	33.1	0.73	5.24	5.97	1.28	14.67	1.28	17.23	9.47
D700	23.6	0.70	5.09	5.79	1.16	14.66	2.30	18.13	24.15
Dov2	34.0	0.79	5.22	6.01	1.20	13.89	1.50	16.58	11.56
Dov3	15.9	0.64	4.52	5.15	1.10	12.34	1.25	14.68	7.98
Dov4	51.6	0.64	4.23	4.87	1.17	14.26	2.12	17.55	29.47
SD1	28.8	0.62	-	-	0.82	13.79	0.37	14.98	7.01
SD2	86.5	-	-	-	2.36	19.47	2.75	24.57	6.19
SCH1	23.2	0.37	-	-	1.39	11.09	0.56	13.04	5.06
SCH2	16.1	0.22	-	-	2.57	11.83	2.09	16.49	4.92
SCH3	67.7	1.21	-	-	0.03	24.45	2.76	27.24	8.94
SCH4	66.9	1.21	-	-	0.41	26.76	5.16	32.33	10.39
SCH5	18.7	0.81	-	-	0.03	18.36	0.94	19.33	7.52
SCH6	18.7	0.84	-	-	0.02	18.24	0.91	19.17	7.74
SCH8	407.4	0.42	-	-	0.70	14.37	6.32	21.38	28.92
SC1	140.0	0.29	-	-	0.74	10.78	5.56	17.08	15.65
SC2	73.7	0.26	-	-	1.45	13.18	7.93	22.56	15.81

Looking at the phosphorus compounds in the ports it can be seen that the RDP concentration was highest at point Cal 2 (12.97) whereas at the remaining points the concentrations varied between 0.15 (C5) and 1.21 µmol L^{-1} (C3). At point Cal 2 also high silicate, nitrate nitrite and ammonium concentrations were observed. As this point is situated at the service quay in an enclosed position at the eastern end of the harbour this point is easily eutrophicated. Inside the harbour of Calais the nitrate, silicate and ammonium concentrations were slightly increased in comparison to the samples taken in Dover, whereas in Dover the nitrite concentrations were increased. The reason therefore might be the architecture of the ports. Dover has one big “basin” open at two sides and no freshwater inflow. During each ebb and flow the water is flowing through the port and enables a marked water

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exchange. Additionally a great part of the harbour cannot be reached from the public areas. The opposite holds for Calais. The port has many enclosed arms and areas. Water exchange is only possible through the relatively small gate in the west of the port. Additionally the city Calais was built around the harbour and therefore the anthropogenic influence is greater than in Dover.

Inside the seawater scrubber system the RDP concentrations were only higher at points SCH3 and SCH4. At the remaining points the determined concentrations were within the range observed inside the harbour. Comparing the inlet and outlet samples an increase in nitrate, nitrite and ammonium can be seen. In contrast inside the system especially the NO_2^- and NH_4^+ values are low and even lower than those observed in the outlet. Only the nitrate concentrations are slightly increased inside the seawater scrubber due to the NO_x remove from the fluegas.

8.5.4 Polycyclic Aromatic Hydrocarbons

The PAH concentrations determined for the samples taken in November are shown in Table 69,,Table 70 and Table 72. From the PAH concentrations measured in the samples taken in Calais it can be seen that the lowest total amount was determined for point Cal 2 (225 ng L^{-1}) and the highest for C 350 (625 ng L^{-1}). In Dover the lowest concentration was measured at point D 0 (106 ng L^{-1}) and the highest at point Dov 3 (569 ng L^{-1}). The transect samples taken in Dover and Calais indicate a specific trend. In Dover the samples taken 50 m away from the outlet showed the highest concentration and in Calais that one 350 m away from the outlet. Compared to the previous samplings, the highest concentrations were observed.

Taking a look at the seawater scrubber samples the highest amount was again determined inside the settling tank. Here high concentrations of phenanthrene, fluoranthene, pyrene, chrysene and benz[*a*]anthracene were measured. Also high concentrations of high molecular weight PAHs were observed, whereas two-ring compounds were not enriched. As these compounds have a high solubility and do not adsorb to surfaces, they are not removed by the cyclones. The concentrations in the seawater scrubber outlet are within the same range as observed during the other samplings.

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Quality of measurement: Comparison 1st and 2nd extraction

The regressions of the filter weights and the regression of all PAH concentrations determined for the first and the second extraction of the samples are shown in Fig. 37. It can be seen that both values are close to one and no outlyers are obvious.

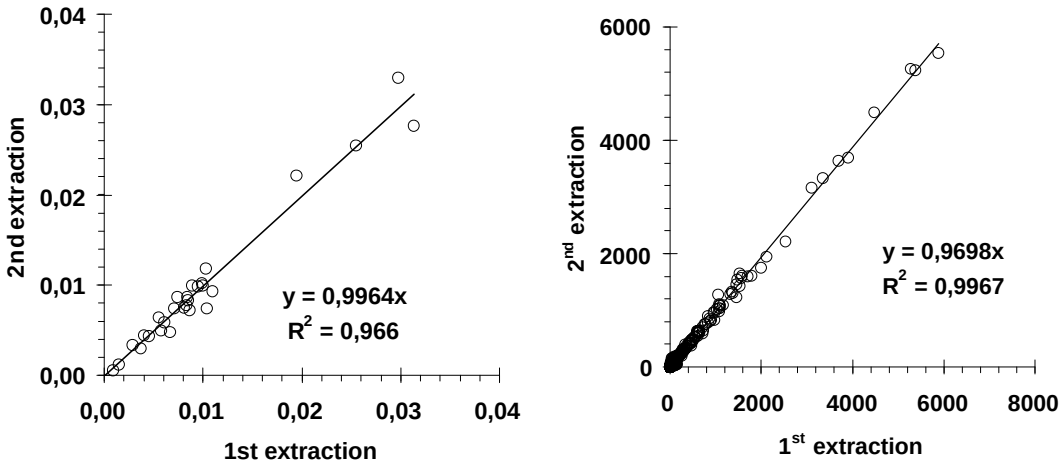

Fig. 37: Regression between the first and the second extraction. Left: filter weights, right: PAH concentrations.

Origin of PAHs

To determine the relationships between the different sampling points and to determine the origin of the PAHs a regression analysis of the compounds (Table 63) and of the sampling points (Table 64) was performed. Additionally a principle component analysis was carried out (Table 66 and Fig. 39) and a plot of the isomeric ratios Phen/Anth and Flua/Pyr (Fig. 38) and BaA/Chry (Table 65) was drawn.

Looking at Table 63 it can be seen that nearly all compounds are highly correlated. Only anthracene and acenaphthene show moderate R^2 values. To obtain a better resolution and to prevent mathematical errors a look at Table 64 is necessary. From this it can be stated that all Calais samples with the exception of Cal 2 show the same distribution of PAHs. Also the seawater scrubber samples (without the inlet samples) are highly correlated with each other. Additionally the points Dov 4 and D50 seem to show different PAH patterns in comparison to the remaining samples taken in Dover. No correlation was observed between the samples taken from the seawater scrubber and those taken in Calais, between the seawater scrubber samples and those taken in Dover, and also between most samples taken in Dover and Calais. In summary it can be said, that the PAH composition inside the harbours was different from that in the seawater scrubber system with one exception: point D5 which was taken directly in front of the seawater scrubber outlet is highly correlated with the seawater scrubber samples. A comparably high correlation was not observed in Calais or at the remaining transect points in Dover.

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Table 63: Regression of PAH compounds. Colours are added for a better visualisation. Yellow - highly correlated, orange and red - moderate or low correlation, dark red - no significant correlation.

	ATHY	ATHE	FLRE	PHEN	ANTH	FLUA	PYR	BaA	CHRY	BbkF	BaP	DahA	BghiP	INDE
ATHY	1	0.865	0.926	0.906	0.93	0.868	0.913	0.92	0.899	0.903	0.928	0.813	0.82	0.757
ATHE		1	0.724	0.696	0.831	0.684	0.718	0.78	0.729	0.781	0.761	0.601	0.615	0.557
FLRE			1	0.996	0.906	0.976	0.993	0.969	0.984	0.968	0.985	0.952	0.961	0.908
PHEN				1	0.874	0.967	0.986	0.974	0.989	0.965	0.989	0.962	0.956	0.894
ANTH					1	0.897	0.926	0.876	0.869	0.892	0.89	0.786	0.848	0.831
FLUA						1	0.984	0.939	0.968	0.967	0.949	0.964	0.991	0.968
PYR							1	0.961	0.977	0.966	0.976	0.947	0.965	0.926
BaA								1	0.991	0.987	0.99	0.937	0.915	0.842
CHRY									1	0.988	0.989	0.97	0.955	0.893
BbkF										1	0.979	0.946	0.945	0.89
BaP											1	0.934	0.925	0.853
DahA												1	0.973	0.929
BghiP													1	0.983
INDE														1

Table 64: Regression of sampling points. Colours are added for a better visualisation. Yellow - highly correlated, orange and red - moderate or low correlation, dark red - no significant correlation.

	Cal1	Cal2	Cal3	Cal4	C0	C5	C50	C350	C700	D5	D50	D350	D700	Dov2	Dov3	Dov4	D0	SD1	SD2	SCH1	SCH2	SCH3	SCH4	SCH5	SCH6	SCH8	SC1	SC2	
Cal1	1	0.196	0.878	0.956	0.892	0.927	0.954	0.77	0.968	0.507	0.895	0.542	0.438	0.72	0.556	0.752	0.393	0.913	0.468	0.928	0.367	0.334	0.382	0.359	0.355	0.373	0.951	0.421	Cal1
Cal2		1	0.306	0.246	0.261	0.232	0.239	0.272	0.264	0.466	0.223	0.531	0.616	0.513	0.315	0.201	0.689	0.251	0.243	0.144	0.245	0.239	0.23	0.241	0.239	0.24	0.285	0.252	Cal2
Cal3			1	0.929	0.928	0.96	0.96	0.965	0.907	0.717	0.916	0.78	0.654	0.887	0.836	0.823	0.605	0.855	0.653	0.737	0.573	0.546	0.589	0.573	0.562	0.604	0.925	0.632	Cal3
Cal4				1	0.945	0.914	0.946	0.841	0.986	0.608	0.845	0.618	0.532	0.781	0.632	0.692	0.502	0.94	0.543	0.89	0.448	0.414	0.463	0.433	0.43	0.45	0.96	0.488	Cal4
C0					1	0.891	0.905	0.853	0.938	0.765	0.816	0.735	0.663	0.865	0.737	0.659	0.601	0.963	0.753	0.85	0.663	0.628	0.678	0.647	0.646	0.657	0.974	0.695	C0
C5						1	0.991	0.925	0.892	0.615	0.98	0.698	0.539	0.823	0.775	0.909	0.474	0.833	0.575	0.761	0.486	0.46	0.499	0.494	0.482	0.52	0.919	0.567	C5
C50							1	0.901	0.928	0.603	0.97	0.669	0.527	0.814	0.723	0.871	0.472	0.873	0.551	0.802	0.46	0.431	0.472	0.462	0.451	0.484	0.944	0.532	C50
C350								1	0.792	0.714	0.876	0.78	0.628	0.843	0.909	0.835	0.572	0.734	0.656	0.594	0.592	0.575	0.608	0.602	0.588	0.644	0.818	0.661	C350
C700									1	0.589	0.831	0.607	0.533	0.776	0.589	0.667	0.507	0.951	0.528	0.934	0.429	0.393	0.446	0.412	0.411	0.426	0.969	0.464	C700
D5										1	0.548	0.903	0.924	0.893	0.807	0.454	0.853	0.691	0.904	0.434	0.896	0.88	0.887	0.884	0.883	0.888	0.698	0.896	D5
D50											1	0.662	0.49	0.784	0.739	0.956	0.42	0.767	0.513	0.701	0.43	0.405	0.439	0.444	0.429	0.468	0.872	0.52	D50
D350												1	0.943	0.943	0.897	0.618	0.896	0.793	0.783	0.427	0.768	0.755	0.756	0.776	0.766	0.79	0.707	0.813	D350
D700													1	0.89	0.76	0.416	0.963	0.591	0.78	0.374	0.782	0.768	0.765	0.773	0.771	0.774	0.627	0.783	D700
Dov2														1	0.861	0.695	0.82	0.801	0.793	0.601	0.742	0.72	0.74	0.742	0.735	0.753	0.859	0.789	Dov2
Dov3															1	0.741	0.672	0.58	0.78	0.396	0.757	0.755	0.763	0.782	0.765	0.819	0.674	0.826	Dov3
Dov4																1	0.348	0.577	0.419	0.519	0.354	0.339	0.36	0.381	0.361	0.41	0.7152	0.458	Dov4
D0																	1	0.538	0.65	0.347	0.652	0.636	0.636	0.637	0.636	0.641	0.572	0.645	D0
SD1																		1	0.66	0.908	0.563	0.522	0.575	0.537	0.54	0.539	0.975	0.583	SD1
SD2																			1	0.429	0.988	0.978	0.991	0.982	0.984	0.977	0.655	0.982	SD2
SCH1																				1	0.327	0.291	0.345	0.307	0.31	0.31	0.892	0.35	SCH1
SCH2																					1	0.998	0.997	0.996	0.998	0.99	0.559	0.985	SCH2
SCH3																						1	0.995	0.997	0.999	0.991	0.522	0.983	SCH3
SCH4																							1	0.993	0.995	0.99	0.57	0.981	SCH4
SCH5																								1	0.999	0.996	0.546	0.993	SCH5
SCH6																									1	0.993	0.543	0.989	SCH6
SCH8																										1	0.554	0.991	SCH8
SC1																											1	0.603	SC1
SC2																												1	SC2

Table 65: Isomeric ratios of benz[*a*]anthracene and chrysene

sampl. point	Cal 1	Cal 2	Cal 3	Cal 4	C0	C5	C50	C350	C700
BaA/CHRY	0.9	0.8	0.7	1.0	0.9	1.3	0.8	0.8	0.9

sampl. point	Dov 2	Dov 3	Dov 4	D0	D5	D50	D350	D700
BaA/CHRY	0.8	0.8	0.8	0.8	0.8	0.7	0.9	0.9

sampl. point	SD1	SD2	SCH1	SCH2	SC1	SC2	SCH3	SCH4	SCH5	SCH6	SCH8
BaA/CHRY	1.7	1.9	1.0	0.5	0.8	0.6	0.5	0.5	0.5	0.6	0.5

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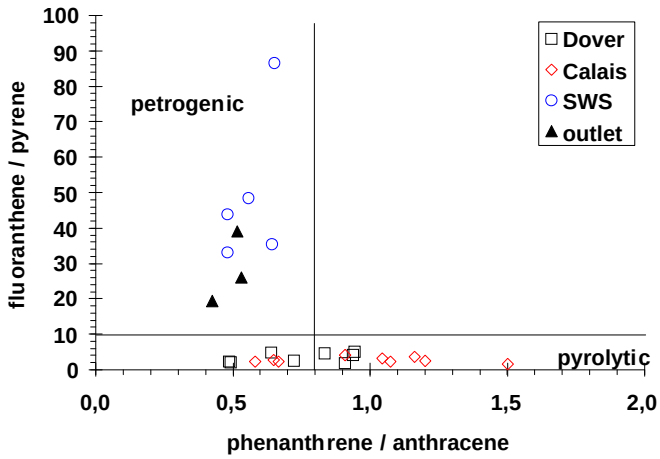

Fig. 38: Plot of isomeric phenanthrene/anthracene ratios against fluoranthene/pyrene ratios for all samples

Taking a look at the BaA/Chry ratios (Table 65) it can be seen that all values, with exception of SD1, SD2 and D5 are <1 and therefore indicate a pyrolytic origin. In Fig. 38 where the phenanthrene/anthracene and fluoranthene/pyrene ratios are plotted, only the samples taken from the seawater scrubber outlet and the seawater scrubber system itself show petrogenic character. The remaining samples, especially those taken in Calais, seem to originate from combustion processes. As the samples were taken in fall when the heating season starts, these PAHs are most probably PAHs produced by burning wood, heating oil and gas.

The principal component plot shows the similar separation of the samples as the regression chart already did. Sample Cal 2 is an outlyer, showing only low concentrations. Dov 2 is correlated with C700, C350 and C005 and these samples are also located in one group in the PCA plot. Additionally D50, SD1 and Cal1 are within this group. All these samples show negative values for eigenvector 2 which is positive for low molecular weight and negative for high molecular weight PAHs. The samples show a similar distribution but as eigenvector 2 is only responsible for 20 % of the total variance it is not significant. According to their distribution along eigenvector 2 the samples can partially be divided into PAHs originating from petrogenic (negative) or pyrolytic (positive) pollution sources. Thereafter D50 has the most petrogenic and Cal 4 and C 700 the most pyrolytic character. This can easily be explained by the positions of these points. Cal 4 and C 700 are the most eastern points in the port Calais and are situated at the entrance. These points are therefore influenced by North Sea water reaching the harbour. There the main pollution source is the atmosphere, which carries especially PAHs from pyrolytic processes. Inside the port the influence of the shipping activities is greater and this direct pollution is of petrogenic origin.

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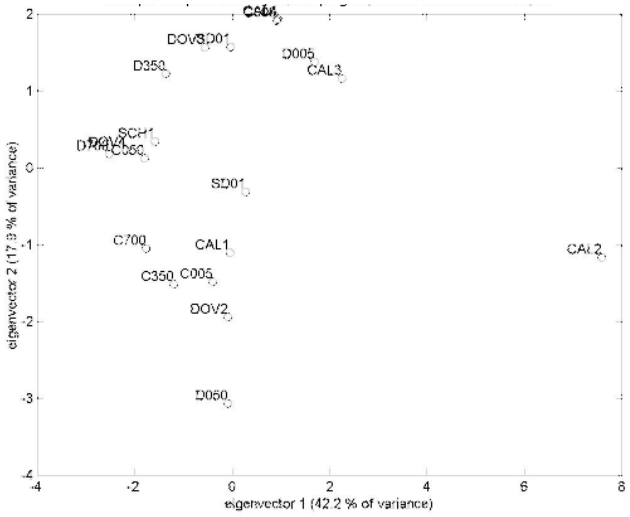

Fig. 39: Results of the PCA of the harbour samples

Table 66: Feature vector for the PCA of the harbour samples

	39.6 % (14.0)	22.3 % (14.0)
acenaphthylene	0.13	0.38
acenaphthene	-0.13	0.42
fluorene	-0.09	0.54
phenanthrene	0.23	0.36
anthracene	0.28	0.35
fluoranthene	0.32	0.18
pyrene	0.32	0.11
benz[*a*]anthracene	0.36	-0.14
chrysene	0.38	-0.14
benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0.41	-0.12
benzo[*a*]pyrene	0.40	-0.14
dibenz[*a,h*]anthracene	0.14	-0.06
benzo[*ghi*]perylene	0.02	-0.11
indeno(*1,2,3,c,d*)pyrene	0.13	0.38

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8.6 Annual circle

8.6.1 pH, salinity and temperature

In this chapter the temperature, salinity and pH values determined during all samplings are shown. Inside the “Pride of Kent“ not at all points samples were taken during every sampling. In February the seawater scrubber was not active and therefore only samples from the inlet and outlet were taken. During the sampling in July sampling points 4, 7 and 8 were closed and in September and November the settling tank was not full enough to take a sample from point 7. For samples taken inside the harbour of Calais (Fig. 40, ,Fig. 41) values for all samplings are available. It can be seen that the highest temperatures were measured in late summer during the sampling in September. Here the water temperature was about 22 °C and thus about 15 °C higher than during the sampling in February. The salinity at point Cal 4 was relative stable and higher than at point Cal 1 to Cal 3. This point is situated close to the harbour entrance and is therefore influenced by the North Sea where the salinity is relatively stable. The farer inside the sampling point was located in the harbour the higher the variability was. At point Cal 2 at the eastern end of a long sidearm the salinity varied within a wide range (18.3 to 34.0). As the pH in brackish and fresh water is lower than in salt water, the pH was also very variable at this point (7.76 - 8.50).

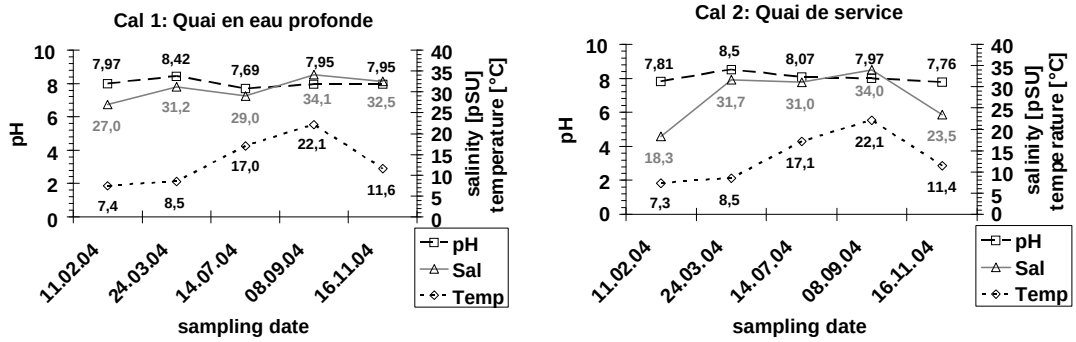

Fig. 40: Salinity, temperature, and pH measured at points Cal 1 and Cal 2

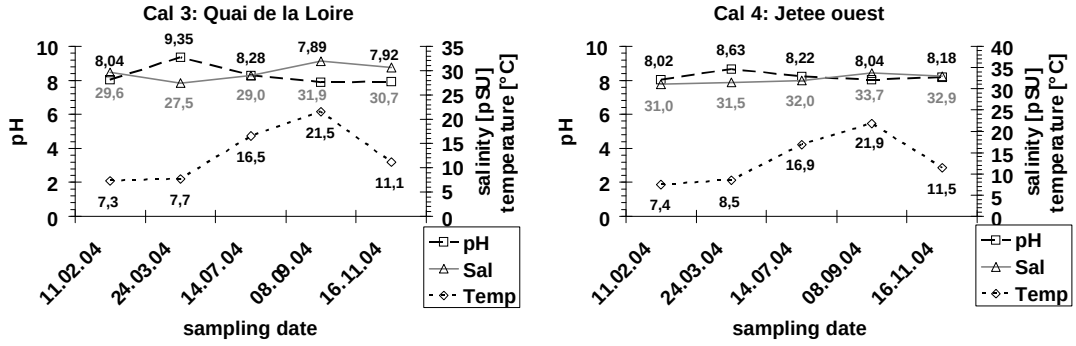

Fig. 41: Salinity, temperature, and pH measured at points Cal 3 and Cal 4

Samples from the transect points in Calais were only taken in July, September and November. The annual course is shown in Fig. 43 and Fig. 44. As these points were situated inside the harbour the

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variability in salinity and pH was lower than in the samples taken closer to the shore. The latter are characterised by lower water depths and reduced water exchange and therefore by higher possibilities for the formation and longer duration of a stratified water body. The temperature at the transect points was also highest in September and decreased towards November. Only during the sampling in July an increase in pH from point C5 to C700 was observed. During that sampling also a salinity increase was observed.

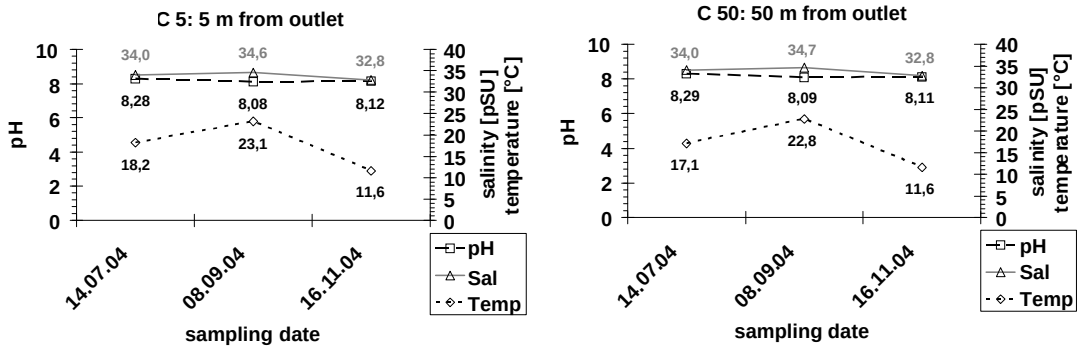

Fig. 42: Salinity, temperature, and pH measured at points C5 and C50

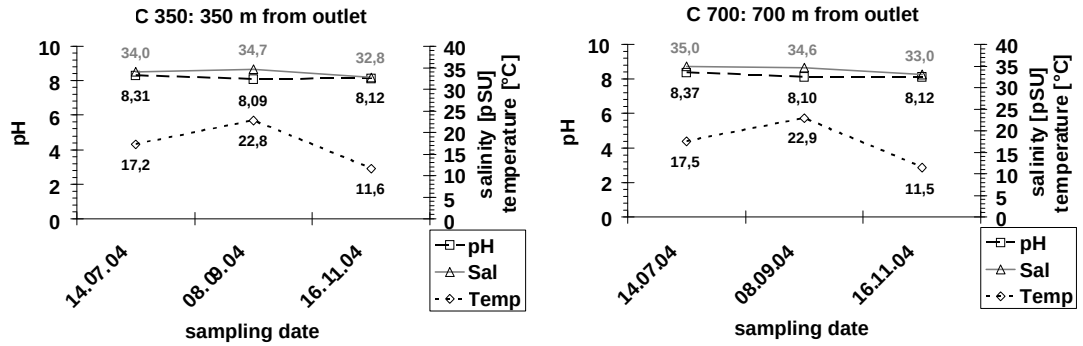

Fig. 43: Salinity, temperature, and pH measured at points C350 and C750

The results of the pH, salinity and temperature measurements of Dover are shown in Fig. 44 and Fig. 45. The results of the transect samples are shown in Fig. 46 and Fig. 47. In Dover the variability in pH and salinity was lower than in Calais. As mentioned before, this is mainly due to the differences in the architecture of the two ports. Calais is an enclosed harbour with three separated arms and only one entrance. The harbour is situated parallel to the stream which enables a water exchange mainly in that part of the harbour close to the entrance. In the remaining part of the harbour, especially at the end of the three arms ebb and flow are the only forces allowing a water exchange inside the port. Opposite to Calais, the port of Dover is relatively open. There are two entrances, one in the north-west and one in the north-east. The stream, which is flowing parallel to the harbour, has the chance to flow partially through the harbour. Therefore a high water exchange is possible and the influence of the North Sea is greater here than in Calais. The lowest measured salinity was 34 PSU. Temperature was highest in September and about 14 °C higher than in February. During all samplings the temperatures in Dover were about 1 °C higher than in Calais. The values determined at the transect sampling points are within the same range as the samples taken at the remaining points.

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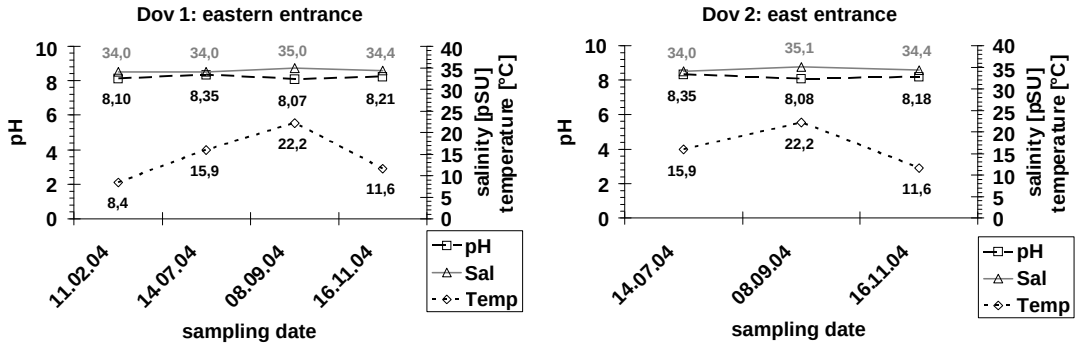

Fig. 44: Salinity, temperature, and pH measured at points Dov 1 and Dov 2

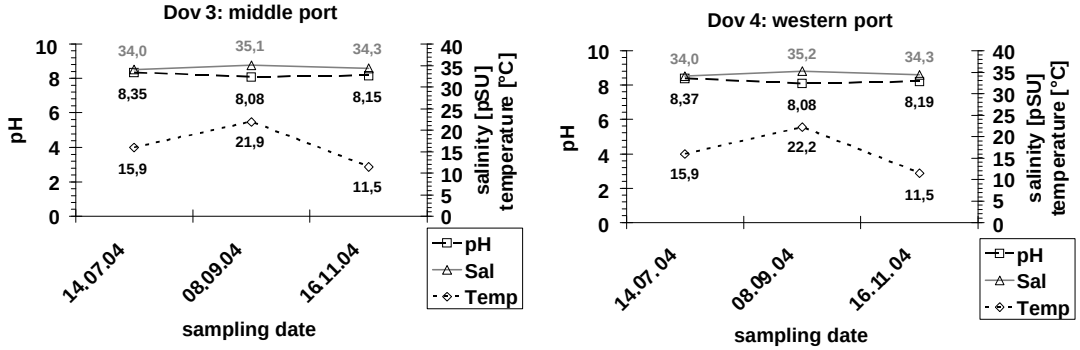

Fig. 45: Salinity, temperature, and pH measured at points Dov 3 and Dov 4

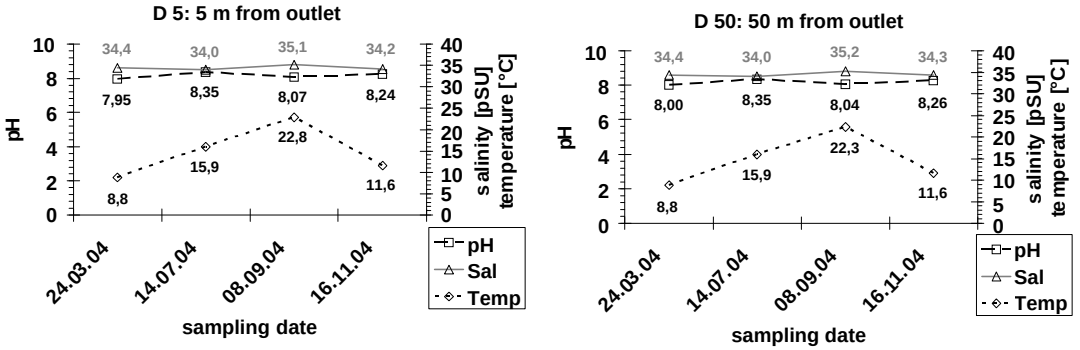

Fig. 46: Salinity, temperature, and pH measured at points D5 and D50

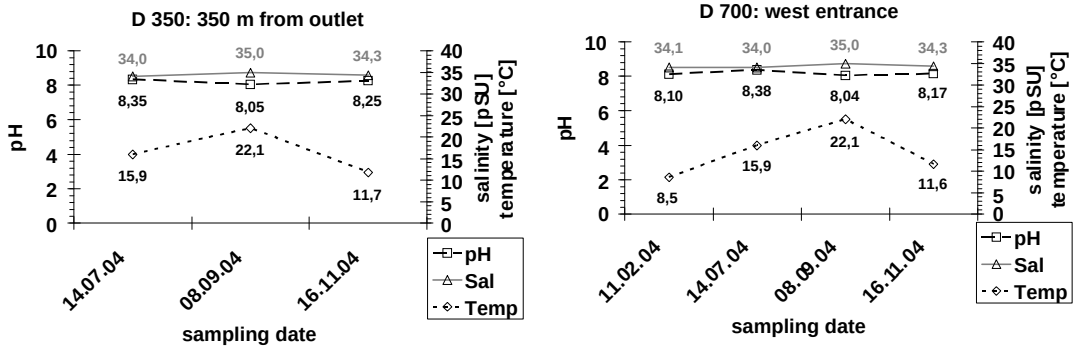

Fig. 47: Salinity, temperature, and pH measured at points D350 and D700

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Table 67: Differences between the inlet and outlet samples taken from the seawater scrubber system in Calais, Dover and the Channel. Left: pH difference. Right: temperature difference

pH	March	July	Sept.	Nov.
Dover	0.43	1.51	1.79	1.85
Channel	1.16	1.45	1.68	1.62
Calais	0.66	1.34	1.73	1.48

Temp [°C]	March	July	Sept.	Nov.
Dover	4.1	2.9	13.6	14.2
Channel	1.9	2.8	14.1	12.2
Calais	3.3	2.7	16.9	11.9

The annual course of the salinity, pH and temperature of the inlet and outlet samples is shown in Fig. 48 (Dover), Fig. 49 (Calais) and Fig. 50 (Channel). The pH, the temperature and the salinity of the inlet samples taken in Dover and Calais are within the same range as the samples taken in the ports. Only the sample taken in Calais in September shows a relatively low pH, but this is comparable to the sample taken at point Cal 2 (Table 49). As the samples from point SC1 were not taken at the same time and not directly at the pier but during entering the harbour, small variations are possible. Therefore it can be said, that the values are comparable and an influence of the outlet water onto the inlet water can be mainly excluded. Looking at the outlet samples, also an annual influence onto the temperature is obvious. The temperature of the outlet is strongly dependent of the inlet temperature. but as the difference between the inlet and outlet temperatures was greater in September and November than during the samplings in February, March and July (Table 67) the main influence is by the seawater scrubber.

The lowest pH in the outlet was measured in September as well. The reason therefore might also be differences in the efficiency of the Ecosilencer. Another reason could be the relatively high temperature of the effluent, because the pH is also temperature dependent. To determine this dependency a small test was performed. 500 mL seawater (Jade Bay, Table 1) were heated and cooled down again and the pH was measured continuously. It can be seen that the higher the temperature was, the lower the pH was. The different ascent between heating and cooling is a physical effect called hysteresis. If calcium carbonate is dissolved in water the following reaction occurs:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$$

An increase in the temperature shifts the equilibrium towards the left side. Therefore more CO_2 is introduced and carbonic acid is built according to:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2\,H^+ + CO_3^{2-}$$

This reduces the pH. When the water is cooled down again the CO_2 solubility increases and carbonic acid concentration is reduced, resulting in a pH increase. As during the heating process the CO_2 has to leave the water this step takes more time in comparison to the increase in solubility.

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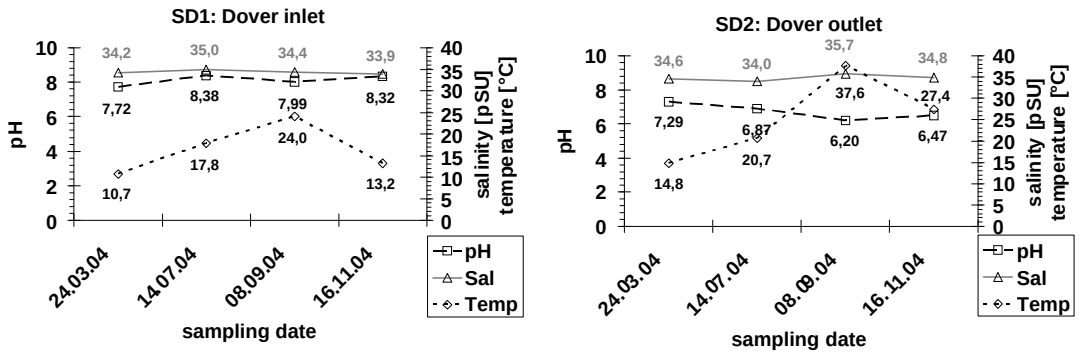

Fig. 48: Salinity, temperature, and pH measured at points SD1 and SD2

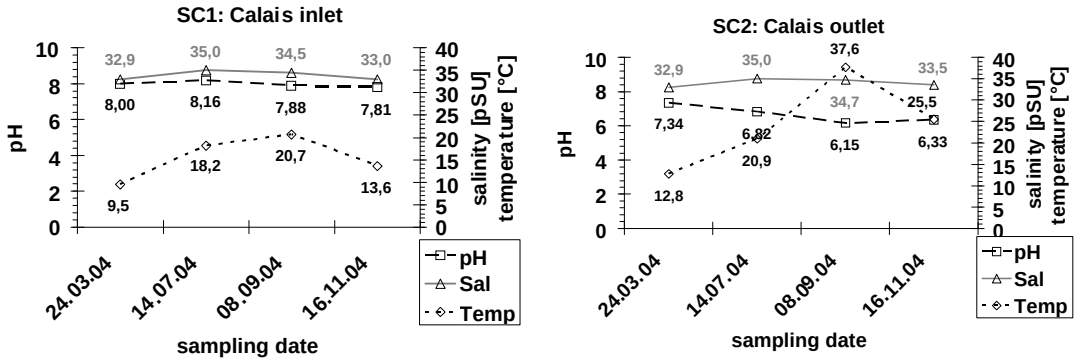

Fig. 49: Salinity, temperature, and pH measured at points SC1 and SC2

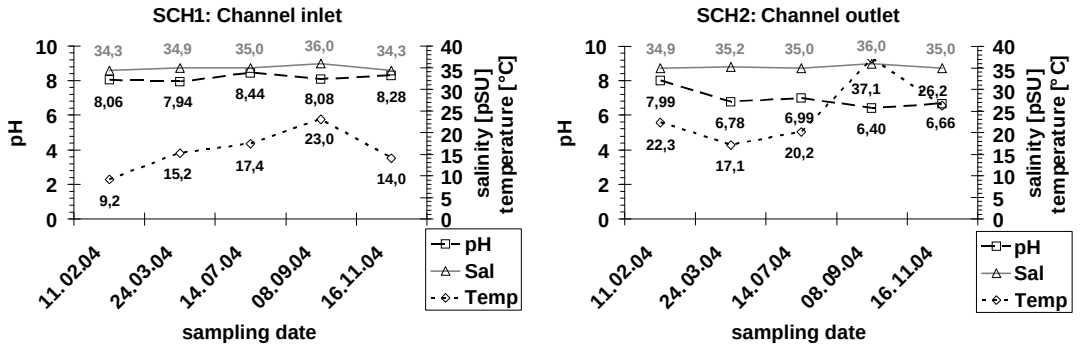

Fig. 50: Salinity, temperature, and pH measured at points SCH1 and SCH2

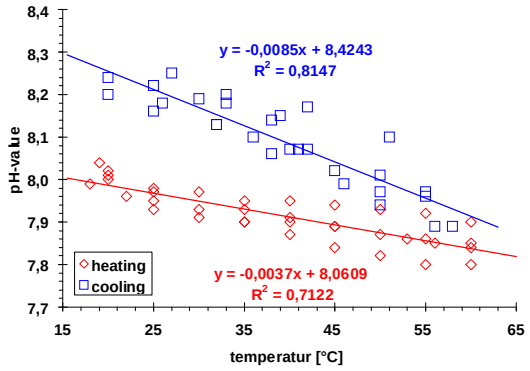

Fig. 51: Temperature dependency of pH. The red line shows the course of the pH when the sample was heated and the blue line shows the course of the pH when the sample was cooled down again.

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The comparison of all samples taken at the points SCH3, SCH5 and SCH6 are shown in Fig. 52 and Fig. 53. The salinity in these samples was always relatively high in comparison to the samples taken inside the harbours and was highest in September. In September also the highest temperature was measured. The lowest pH was determined in the samples taken during the second sampling. As the system was not working completely in March the reason could be a slower flow speed of the water through the Ecosilencer and therefore a higher saturation with sulphuric and nitric acid.

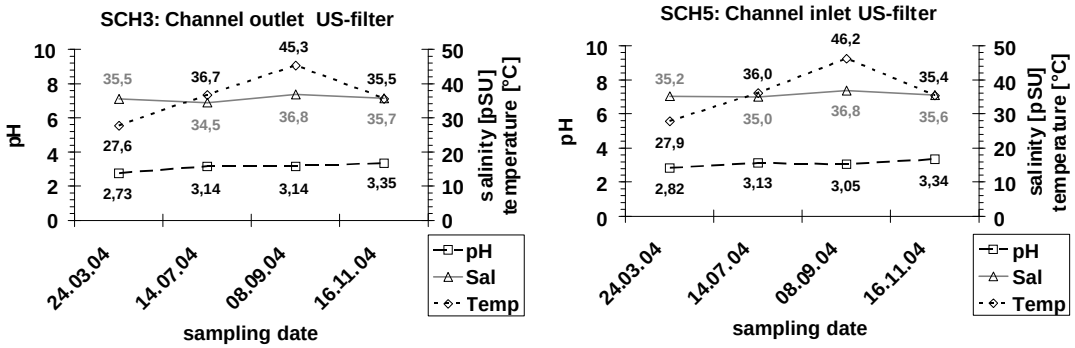

Fig. 52: Salinity, temperature, and pH measured at points SCH3 and SCH5

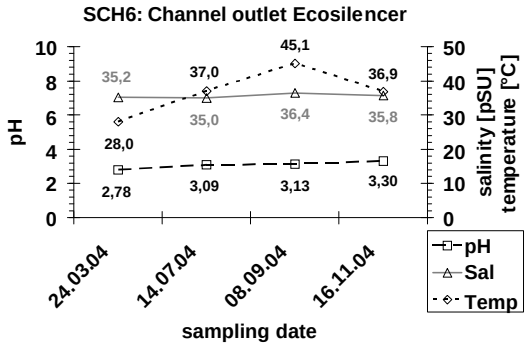

Fig. 53: Salinity, temperature, and pH measured at point SCH6

A plot of all pH values observed during all sampling is shown in Fig. 54 and Fig. 55. The error bars show the maximum allowed pH change caused by effluents outside the initial mixing zone (US-EPA 1986). In both graphs it can be seen that the natural pH range is greater than the pH change within the sample suite taken at the transect points. The same can be seen in Fig. 56. During no sampling a pH decrease from the first transect point towards the harbour entrance was observed.

From Fig. 58 where all the measured temperatures of all sampling points (without seawater scrubber system) are shown, it can be seen that the highest temperature differences were observed inside the ports in March. The temperatures measured at the transect points in July were partially higher than those measured at the remaining points inside the harbour. In detail this is shown in Fig. 57. It can be seen that during the sampling in July and September the temperatures were higher at the first transect point in comparison to the remaining points. During the sampling in September the difference between the inlet and the outlet temperature was also very high (Table 67). In July the difference was over

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10 °C lower and the same effect was observed whereas in November high temperature differences did not increase the values at points C5 and D5. Due to the buoyancy of the warmer effluent it will initially have an effect on the upper water column. In summer the density stratification is more stable than in winter or fall. Therefore the influenced water volume is smaller in summer than in winter and the temperature can be influenced more easily. As this temperature increase made up only 1 °C and was only measured close to the ship, no negative effects are to be expected.

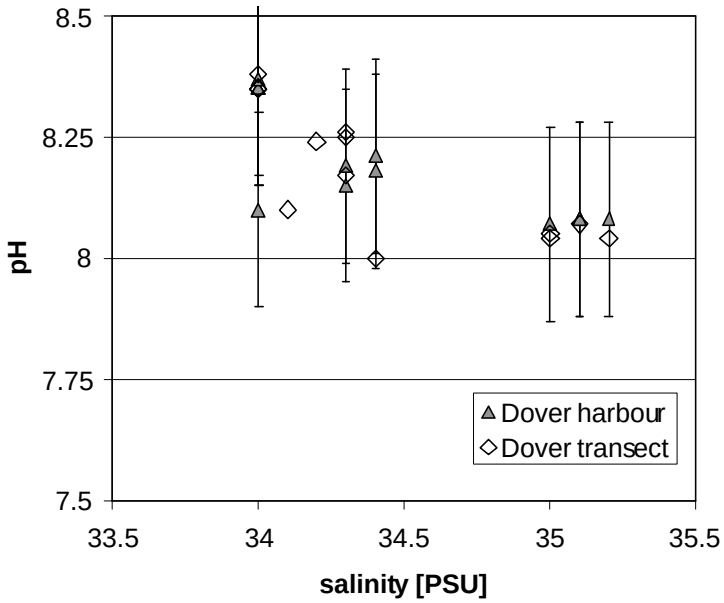

Fig. 54: pH and salinity in the harbour of Dover. Triangles represent the natural variability during all samplings in 2004. Diamonds represent the values of the transect samples.

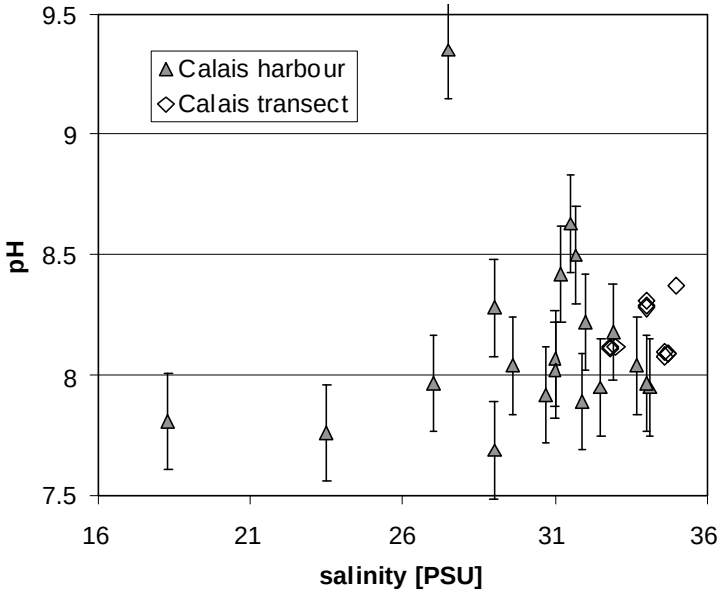

Fig. 55: pH and salinity in the harbour of Calais. Triangles represent the natural variability during all samplings in 2004. Diamonds represent the transect values.

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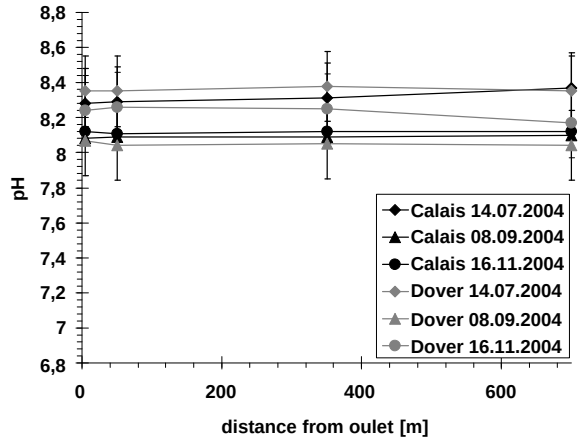

Fig. 56: pH impact of SWS effluents on the receiving harbour water in Dover and Calais at three sampling (July, Sept. and Nov.)

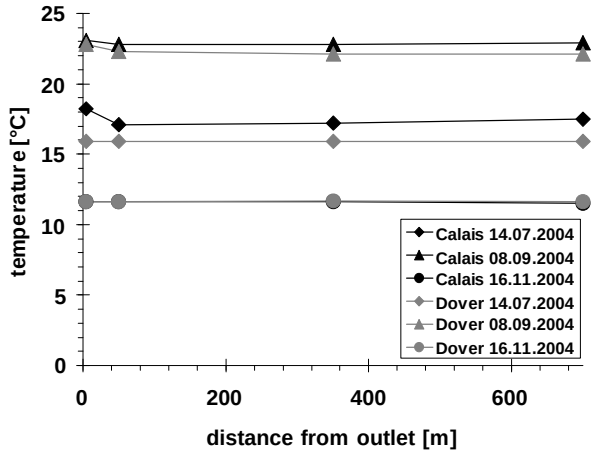

Fig. 57: Temperature [°C] impact of SWS effluents on the receiving harbour water in Dover and Calais at three sampling (July, Sept. and Nov.)

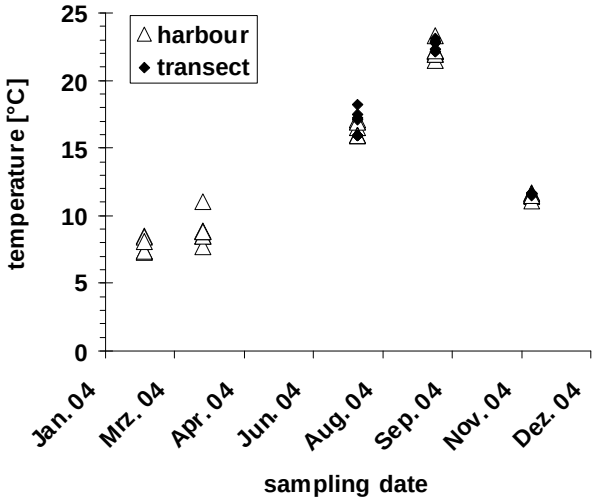

Fig. 58: Temperatures [°C] of harbour and transect samples.

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8.6.2 Nitrate and sulphate

Nitrate

In Fig. 59 the nitrate concentrations determined in the ports and for the inlet and outlet samples are shown. It can be seen that in summer the concentrations were lower than in winter and fall. Because nitrogen is an essential compound for marine primary production it is depleted in summer when the phytoplankton production is high and nitrogen availability is a limiting factor. In winter when the plankton production is generally close to zero the nitrogen is remineralised and its concentration increases. Additionally in Fig. 59 the nitrate concentrations of the inlet and the outlet water are shown. It can be seen that in Calais the outlet concentration was within the natural range whereas in Dover it was slightly higher. The transect points did not show a nitrate concentration increase during any sampling and were all within the natural range.

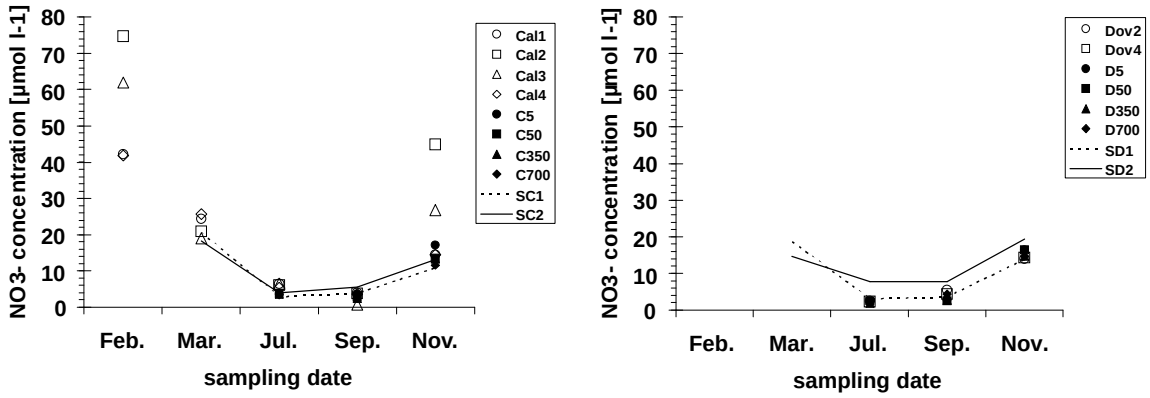

Fig. 59: Nitrate concentrations [µmol l^{-1}] observed during all samplings. Left: Port of Calais. Right: Port of Dover

The sulphate concentrations determined in the inlet and outlet of the seawater scrubber samples are shown in Table 68. Calculating the sulphate increase between the inlet and the outlet it can be seen that the greatest difference was observed during the sampling in November in Dover. This increase of 165 pm corresponds to a concentration change of 6.1 %. This value lies within the accuracy of the measurement and within the natural variability.

Table 68: Comparison of sulphate inlet and outlet concentrations [ppm]

	Feb.	Mar.	Sep.	Nov.
SD1	n.d.	2949	n.d.	2699
SD2	n.d.	2962	2710	2864
SCH1	2842	2990	2590	2685
SCH2	2874	3052	2600	2805
SC1	n.d.	2920	n.d.	2587
SC2	n.d.	2938	2870	2644

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8.6.3 Polycyclic aromatic hydrocarbons

Within this chapter the PAH concentrations determined during all samplings will be discussed. Table 69 shows the total PAH amounts, Table 70 the particulate and dissolved fractions of the harbour samples and Table 72 the bound and unbound PAHs of the seawater scrubber samples. Looking at the total amounts which are calculated as the sum of the 16 EPA PAHs without naphthalene, it can be seen that the lowest concentrations were measured in July and the highest in November. This is an effect of fossil fuel and wood burning in the cities around the ports. Parallel to this seasonal effect there are also great differences between the two harbours and within harbours themselves. As an effect of the harbour structure as explained above in Dover generally lower concentrations than in Calais were observed. Water from outside the harbour, which is normally less contaminated and less subjected to anthropogenic influence, can easier reach the port of Dover than the port of Calais.

Besides physical processes such as water exchange rates chemical and biological processes control the PAH contents in natural waters. Phytoplankton and seston adsorb PAHs and thus become passively enriched. Additionally, organisms can take up the PAHs and change their structure or destroy specific structures leading to an enrichment of some structures whereas others are depleted. Additionally organisms that have taken up PAHs are removing the PAHs from the water after death when they are sedimenting or when they are consumed by heterotrophic organisms.

With respect to the outlet samples, the contents are always around 3000 ng L^{-1} and the lowest PAH contents were in almost all cases measured in the Channel. The reason for this might be that the cleaning efficiency of the SWS is higher when the machines are running at full speed. Within the seawater scrubber system the highest concentrations were always measured inside the settling tank and at point SCH4. This shows that the cyclones effectively remove particles and hence particle-bound PAHs from the water. In contrary the US filter did not work in all cases. During the sampling in July and September the PAH concentration increased behind the US filter.

Table 69: Sum of all 16 EPA-PAHs (particulate and dissolved, excluding naphthalene) concentrations in ng l^{-1} for all samplings (n.d. = not determined).

	Cal 1	Cal 2	Cal 3	Cal 4	C0	C5	C50	C350	C700	Dov 2	Dov 3	Dov 4	D0	D5	D50	D350	D700	Dover inlet	Dover outlet	Channel inlet	Channel outlet	Calais inlet	Calais outlet
11.02.2004	268	353	209	420	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	246	4055	n.d.	n.d.
24.03.2004	361	334	765	342	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	473	2921	306	3400	282	2380
14.07.2004	99	69	58	46	n.d.	63	46	51	28	41		75	n.d.	26	23	72	39	35	2852	58	2459	60	3395
08.09.2004	117	248	187	134	133	109	65	86	69	130	101	50	n.d.	129	156	70	44	133	3422	72	3263	115	3577
16.11.2004	516	225	327	419	619	622	521	625	428	536	569	419	106	274	345	200	198	432	2870	593	2029	445	3407

	SCH3	SCH4	SCH5	SCH6	SCH7	SCH8
11.02.2004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
24.03.2004	12502	19187	15151	15019	17320	24714
14.07.2004	20354	n.d.	16491	19854	n.d.	n.d.
08.09.2004	16649	23868	14732	15901	n.d.	n.d.
16.11.2004	11879	13486	12465	10334	n.d.	21211

Table 70: PAH concentrations in ng L^{-1}. Listed are the concentrations of the single PAH compounds in all samples. Concentrations are given as dissolved/particulate PAH. Dashes indicate concentrations below the limit of detection. (n.d. = not determined)

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compound	Date	Cal 1	Cal 2	Cal 3	Cal 4	Dov 2	Dov 3	Dov 4	C0	C5	C50	C350	C700	D0	D5	D50	D350	D700	SD1	SD2	SCH1	SCH2	SC1	SC2
ATHY	11.02.04	1/-	4/-	2/-	1/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1/-	-/25	n.d.	n.d.
	24.03.04	2/-	4/-	23/2	8/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1/-	7/-	1/-	9/1	2/-	10/-
	14.07.04	8/-	3/-	9/-	8/-	4/-	n.d.	2/-		-/-	-/-	1/-	-/-		-/-	-/-	-/-	2/-	-/-	6/-	6/-	-/-	-/-	4/-
	08.09.04	1/-	1/-	-/-	1/-	-/-	-/-	-/-	4/-	-/-	-/-	-/-	-/-		-/-	-/-	-/-	-/-	-/-	2/-	-/-	7/-	-/-	3/-
	16.11.04	9/-	8/-	11/-	12/-	28/-	12/-	9/-	9/-	14/-	14/-	12/-	13/-	7/-	8/-	8/-	11/-	10/-	13/-	14/-	8/-	13/-	13/-	23/1
ATHE	11.02.04	7/-	16/-	5/-	6/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5/-	-/120	n.d.	n.d.
	24.03.04	7/-	8/-	15/1	7/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6/-	30/1	5/-	43/3	8/-	32/1
	14.07.04	-/-	8/-	4/-	4/-	2/-	n.d.	5/-	n.d.	3/-	2/-	4/-	3/-		3/-	1/-	2/-	2/-	1/-	28/-	1/-	1/-	2/-	2/-
	08.09.04	5/-	6/-	7/-	3/-	3/-	3/-	3/-	4/-	3/-	2/-	3/-	3/-		3/-	1/-	4/-	2/-	4/-	23/1	3/-	34/1	5/-	45/2
	16.11.04	17/-	72/1	14/-	16/-	45/-	20/-	18/-	19/-	20/-	19/-	21/-	20/-	12/-	18/-	13/-	16/-	19/-	16/-	37/1	12/-	27/1	19/-	60/2
FLRE	11.02.04	25/-	35/-	21/-	25/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25/-	-/518	n.d.	n.d.
	24.03.04	26/-	30/-	74/6	22/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	28/-	132/2	30/-	193/12	23/-	126/4
	14.07.04	5/-	2/-	4/-	1/-	3/-	n.d.	2/-	n.d.	1/-	6/-	5/-	3/-	n.d.	2/-	2/-	3/-	5/-	5/-	113/2	7/-	135/2	6/-	128/3
	08.09.04	5/-	5/-	27/1	6/-	6/-	5/-	6/1	9/-	5/-	8/-	3/-	4/-	n.d.	7/-	7/-	6/-	4/-	9/-	144/5	5/-	147/4	7/-	163/6
	16.11.04	19/-	38/1	14/-	15/-	46/-	31/1	15/-	17/-	20/-	18/-	20/-	18/-	14/-	21/-	13/-	19/-	28/1	17/-	126/4	13/-	108/3	19/-	153/6
PHEN	11.02.04	143/5	184/6	105/6	150/4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	139/3	415/2185	n.d.	n.d.
	24.03.04	152/5	147/5	207/62	134/5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	173/8	964/77	159/6	1039/404	133/4	845/98
	14.07.04	27/1	22/1	3/-	16/-	16/-	n.d.	32/1	n.d.	18/1	18/1	18/-	12/-	n.d.	16/-	14/-	22/1	17/-	13/-	1135/71	23/-	967/68	24/-	1105/121
	08.09.04	36/-	59/3	59/19	43/2	43/1	37/2	15/7	41/2	34/2	23/1	26/1	23/6	n.d.	42/3	73/3	30/1	24/1	45/1	1197/217	33/2	1249/151	47/2	1201/222
	16.11.04	36/2	31/1	43/2	42/3	98/6	127/8	29/2	106/7	59/8	46/4	84/10	41/2	23/2	68/5	29/2	43/3	48/4	63/3	954/140	51/3	760/99	57/5	1087/220
ANTH	11.02.04	12/-	17/1	9/-	11/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11/-	29/152	n.d.	n.d.
	24.03.04	10/-	10/-	21/6	9/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11/1	28/2	11/-	35/13	9/-	22/3
	14.07.04	3/-	3/-	4/-	2/-	1/-	n.d.	1/-	n.d.	2/-	-/-	4/-	1/-	n.d.	-/-	1/-	-/-	1/-	-/-	26/2	3/-	30/2	2/-	41/4
	08.09.04	9/-	9/1	-/-	-/-	16/-	-/-	-/-	-/-	-/-	1/-	1/-	-/-	n.d.	-/-	4/-	1/0	-/-	15/-	30/6	-/-	29/4	-/-	38/7
	16.11.04	16/1	19/1	13/1	17/1	21/1	25/2	14/1	25/2	21/3	20/2	22/3	17/1	12/1	15/1	12/1	17/1	15/1	15/1	24/4	20/1	29/4	20/2	56/11
FLUA	11.02.04	28/1	39/1	20/1	35/1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25/1	72,378	n.d.	n.d.
	24.03.04	29/1	31/1	84/25	41/1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	45/2	163/13	30/1	173/67	29/1	142/17
	14.07.04	18/1	11/-	11/-	6/-	6/-	n.d.	13/-	n.d.	10/-	7/-	7/-	3/-	n.d.	-/-	1/-	9/-	4/-	4/-	121/8	3/-	105/7	5/-	130/14
	08.09.04	27/1	50/3	20/7	16/1	28/1	11/1	-/4	22/1	28/2	9/-	25/1	14/6	n.d.	11/-	35/1	3/0	3/-	19/-	238/43	5/-	188/23	12/-	227/42
	16.11.04	41/2	14/1	46/2	45/3	43/3	97/6	56/3	55/4	67/9	53/5	102/12	41/2	9/3	19/1	36/2	20/1	14/1	20/1	165/24	32/2	119/16	28/2	203/41
PYR	11.02.04	15/10	15/13	6/7	52/17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17/6	94,25	n.d.	n.d.
	24.03.04	35/22	28/14	29/46	36/20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	37/46	232/279	26/16	122/372	22/11	146/262
	14.07.04	12/14	9/7	13/10	5/4	4/2	n.d.	13/5	n.d.	8/7	6/6	6/4	3/2	n.d.	3/2	3/1	9/7	6/2	5/3	213/186	7/2	149/105	10/4	248/236
	08.09.04	20/1	46/3	18/6	23/1	20/1	14/1	-/3	21/1	21/1	9/-	20/1	9/-	n.d.	18/2	29/1	5/0	-/-	12/6	103/383	10/-	348/42	14/-	389/72
	16.11.04	70/4	10/-	44/2	38/2	68/4	103/6	113/7	62/3	103/14	79/8	88/10	38/2	5/7	22/2	73/5	27/2	15/1	18/18	121/246	48/3	225/29	50/4	477/97
BaA	11.02.04	2/1	2/1	6/7	10/3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3/1	5/1	n.d.	n.d.
	24.03.04	7/4	6/3	11/18	7/4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7/9	59/70	3/2	29/88	4/2	40/72
	14.07.04	-/2	-/-	-/-	-/-	-/2	n.d.	-/-	n.d.	-/2	-/-	-/-	-/-	n.d.	-/-	-/-	-/2	-/-	-/-	234/210	-/-	242/170	-/-	355/338
	08.09.04	1/1	7/6	2/7	7/6	3/2	6/6	5/-	5/6	-/-	5/2	1/1	2/-	n.d.	5/7	-/-	4/4	2/1	5/3	57/205	3/2	96/146	5/4	64/216
	16.11.04	49/56	7/5	20/21	29/49	24/36	20/26	21/28	53/56	26/70	27/52	21/48	34/49	4/28	10/13	20/26	7/11	6/11	39/40	95/194	68/97	46/102	28/49	69/201
CHRY	11.02.04	4/3	3/3	3/4	31/10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4/1	23/6	n.d.	n.d.
	24.03.04	22/13	17/9	13/21	18/10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25/31	242/290	7/4	118/361	8/4	109/196
	14.07.04	-/2	2/2	-/-	-/-	-/-	n.d.	-/-	n.d.	-/2	-/-	-/-	-/-	n.d.	-/-	-/-	3/7	-/-	2/2	124/111	4/2	165/116	4/3	191/182
	08.09.04	5/4	8/7	3/8	12/9	4/3	8/8	5/-	8/10	3/5	4/2	1/1	2/-	n.d.	8/11	-/-	5/6	5/3	9/5	101/369	5/4	187/283	10/8	118/403
	16.11.04	54/61	9/6	28/29	30/51	29/44	24/31	26/34	60/64	28/44	32/63	26/59	39/56	5/34	13/17	27/35	7/13	7/13	47/-	153/-	72/101	87/194	34/59	108/315
BbkF	11.02.04	1/1	1/2	1/2	4/7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/1	1/-	n.d.	n.d.
	24.03.04	1/3	1/2	6/17	2/3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/6	4/37	-/-	3/32	2/3	3/26
	14.07.04	-/3	-/-	-/-	-/-	-/-	n.d.	-/-	n.d.	-/4	-/-	-/-	-/-	n.d.	-/-	-/-	-/-	-/-	-/-	-/47	-/-	7/39	-/-	-/56
	08.09.04	-/-	2/11	1/2	1/3	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	n.d.	1/3	-/-	-/-	-/-	-/-	4/95	-/-	17/81	-/-	15/103
	16.11.04	8/32	-/-	4/17	9/29	3/21	4/16	5/18	8/36	3/38	5/37	4/36	4/29	-/18	2/8	3/20	-/3	-/2	6/29	10/72	5/31	7/41	4/27	7/74
BaP	11.02.04	1/3	1/4	1/3	15/25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1/2	5/-	n.d.	n.d.
	24.03.04	3/8	4/8	7/21	3/6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1/27	18/153	1/2	19/183	3/4	16/131
	14.07.04	-/4	-/-	-/-	-/-	-/-	n.d.	-/-	n.d.	-/-	-/-	-/-	-/-	n.d.	-/-	-/-	-/3	-/-	-/-	-/115	-/-	10/63	-/-	13/99
	08.09.04	-/-	2/12	-/-	-/-	-/-	-/-	-/-	-/4	-/-	-/-	-/-	-/-	n.d.	1/4	-/-	-/-	-/-	-/-	6/143	-/-	27/132	-/-	23/152
	16.11.04	6/23	-/-	3/13	7/22	2/12	2/9	4/15	6/27	3/32	4/30	3/30	3/17	-/15	2/9	2/16	-/-	-/-	5/24	14/100	3/20	11/64	3/20	11/125
DahA	11.02.04	-/-	-/1	-/-	-/-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/-	-/-	n.d.	n.d.
	24.03.04	1/2	-/-	4/11	-/1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/3	4/37	-/-	2/23	1/1	3/25
	14.07.04	-/-	-/-	-/-	-/-	-/-	n.d.	-/-	n.d.	-/-	-/-	-/-	-/-	n.d.	n.d.	-/-	-/-	-/-	-/-	-/34	-/-	-/23	-/-	-/42
	08.09.04	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	n.d.	n.d.	-/-	-/-	-/-	-/-	-/3	-/-	2/7	-/-	-/-
	16.11.04	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	1/7	-/-	-/-	-/-	-/3
BghiP	11.02.04	-/1	1/2	-/-	3/5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/-	-/-	n.d.	n.d.
	24.03.04	1/4	1/2	5/14	1/2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/6	5/46	-/1	4/34	1/1	4/31
	14.07.04	-/-	-/-	-/-	-/-	-/-	n.d.	-/-	n.d.	-/4	-/-	-/-	-/-	n.d.	-/-	-/-	-/3	-/-	-/-	-/49	-/-	-/40	-/-	-/62
	08.09.04	-/-	1/4	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	n.d.	-/3	-/-	-/-	-/-	-/-	1/27	-/-	6/29	-/-	9/43
	16.11.04	1/3	-/-	-/-	-/-	-/-	-/-	-/-	-/-	1/6	-/3	1/8	-/-	-/-	2/8	-/-	-/-	-/-	1/3	5/33	-/-	5/27	-/-	3/35
INDE	11.02.04	-/1	-/1	-/-	2/3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/-	-/-	n.d.	n.d.
	24.03.04	1/2	-/1	4/13	1/1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-/2	3/23	-/-	2/16	1/1	2/13
	14.07.04	-/-	-/-	-/-	-/-	-/-	n.d.	-/-	n.d.	-/-	-/-	-/-	-/-	n.d.	-/-	-/-	-/-	-/-	-/-	-/16	-/-	-/13	-/-	-/22
	08.09.04	-/-	1/3	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	n.d.	-/-	-/-	-/-	-/-	-/-	1/17	-/-	4/20	-/-	-/12
	16.11.04	1/3	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-/4	-/-	-/-	2/7	-/-	-/-	-/-	1/3	2/14	-/-	2/11	-/-	1/17

The PAH composition is dominated in all samples by fluorene, phenanthrene and pyrene. Only in a few samples acenaphthene, fluoranthene, chrysene and benz[*a*]anthracene could not be detected. High molecular weight PAHs such as indeno(1,2,3,*c*,*d*)pyrene, benzo[*ghi*]perylene and dibenz[*a,h*]anthracene were below the detection level. Benzo[*a*]pyrene and the sum of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were mainly found in low contents.

As the high molecular weight PAHs are generally more harmful than the low molecular weight PAHs and as the former are more easily degraded by microorganisms it can be stated that the ports of Dover and Calais are not seriously polluted. According to the World Health Organisation the maximum permissible concentration of PAHs in drinking water is 200 ng L^{-1} calculated as the sum of BbF, BghiP,

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BkF, BaP, Flua, Ind in carbon weight. The sums of these compounds are shown in Table 71. It can be seen that in no harbour sample the concentration was higher than the maximum permissible content. Only the PAH concentrations determined directly in the outlet show higher values, but already directly in front of the outlet no increase was observed and values were still below the threshold of 200 ng L^{-1}.

Table 71: Sum of BbF, BghiP, BkF, BaP, Flua, and Inde calculated as carbon weight (n.d. - not determined)

[ng l^{-1}]	Feb.	Mar.	Jul.	Sep.	Nov.
Cal 1	35	50	25	27	114
Cal 2	49	49	10	85	14
Cal 3	27	187	10	29	81
Cal 4	95	58	6	20	109
Dov 2	n.d.	n.d.	6	28	80
Dov 3	n.d.	n.d.	n.d.	11	127
Dov 4	n.d.	n.d.	12	4	96
C0	n.d.	n.d.	n.d.	22	129
C5	n.d.	n.d.	17	32	151
C50	n.d.	n.d.	7	9	130
C350	n.d.	n.d.	7	25	190
C700	n.d.	n.d.	3	19	91
D0	n.d.	n.d.	n.d.	n.d.	43
D5	n.d.	n.d.	0	22	57
D50	n.d.	n.d.	1	34	75
D350	n.d.	n.d.	14	3	23
D700	n.d.	n.d.	4	3	16
SD1	n.d.	85	4	18	89
SD2	n.d.	443	339	547	418
SCH1	29	33	3	5	89
SCH2	433	507	270	502	289
SC1	0	44	5	11	80
SC2	0	367	377	596	492

The PAH composition established in the outlet samples was also found in the seawater scrubber samples. Phenanthrene, fluoranthene and pyrene had the highest contents in all samples. Chrysene and benz[*a*]anthracene were found with contents >2000 ng L^{-1}. The high molecular weight PAHs benzo[*ghi*]perylene, indeno(1,2,3,*c*,*d*)pyrene and dibenz[*a*,*h*]anthracene were almost completely bound to particles and therefore found in highest contents in the settling tank. The low molecular weight PAHs were found almost with equal contents inside the seawater scrubber during all samplings. The variance of the high molecular weight PAH concentrations was however higher. The reason for this might be the particle load of the water entering the seawater scrubber. This was highest in July when also the PAH concentrations were highest.

Table 72: PAH concentrations in ng L^{-1} determined for the seawater scrubber samples. Listed are the concentrations of the single PAH compounds in all samples. Contents are given as dissolved/particulate PAH. Dashes indicate concentrations below the limit of detection. (n.d. = not determined)

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compound	Date	SCH3	SCH4	SCH5	SCH6	SCH7	SCH8
ATHY	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	33/3	39/3	35/4	38/4	34/6	44/9
	14.07.04	41/5	n.d.	32/4	33/4	n.d.	n.d.
	08.09.04	11/1	18/8	8/1	5/1	n.d.	n.d.
	16.11.04	35/3	27/4	38/3	30/3	n.d.	37/9
ATHE	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	166/17	208/17	153/16	170/20	191/33	208/44
	14.07.04	171/22	n.d.	143/17	143/17	n.d.	n.d.
	08.09.04	166/23	143/54	136/20	156/34	n.d.	n.d.
	16.11.04	157/13	107/17	172/13	140/12	n.d.	182/45
FLRE	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	712/75	774/65	809/84	763/88	764/132	815/171
	14.07.04	718/92	n.d.	663/80	648/79	n.d.	n.d.
	08.09.04	650/89	665/250	570/85	553/249	n.d.	n.d.
	16.11.04	596/50	544/86	601/44	493/42	n.d.	880/219
PHEN	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	3972/1445	5052/1423	4644/1594	4382/1757	4469/2229	5308/3276
	14.07.04	7034/1182	n.d.	4766/1907	7122/901	n.d.	n.d.
	08.09.04	4075/2665	3768/4914	3732/2099	3116/3570	n.d.	n.d.
	16.11.04	3666/1599	3334/2374	3798/1503	3139/1341	n.d.	3997/4584
ANTH	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	69/25	118/33	110/38	86/34	82/41	127/79
	14.07.04	138/22	n.d.	98/39	134/17	n.d.	n.d.
	08.09.04	58/38	44/54	85/48	66/89	n.d.	n.d.
	16.11.04	76/33	38/28	115/5	72/31	n.d.	113/129
FLUA	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	619/225	853/240	777/267	691/277	852/425	1269/783
	14.07.04	781/132	n.d.	532/213	769/95	n.d.	n.d.
	08.09.04	743/486	757/991	683/383	200/1005	n.d.	n.d.
	16.11.04	606/264	626/446	647/255	492/210	n.d.	957/1098
PYR	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	491/1358	1176/2553	452/1618	424/1885	700/2119	1179/3490
	14.07.04	861/1592	n.d.	467/1669	1076/1681	n.d.	n.d.
	08.09.04	1313/859	1304/1700	1201/674	263/1816	n.d.	n.d.
	16.11.04	1088/474	960/684	1343/530	1021/436	n.d.	1489/1707
BaA	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	132/364	364/790	138/492	120/534	212/643	312/925
	14.07.04	1298/2397	n.d.	626/2182	1402/2191	n.d.	n.d.
	08.09.04	149/967	155/1480	212/1067	23/1140	n.d.	n.d.
	16.11.04	189/618	168/865	228/618	161/604	n.d.	184/1095
CHRY	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	370/1024	951/2064	448/1603	374/1661	566/1714	835/2472
	14.07.04	492/912	n.d.	249/892	622/970	n.d.	n.d.
	08.09.04	325/2110	335/3271	385/1933	46/2172	n.d.	n.d.
	16.11.04	346/1134	331/1699	423/1162	281/1054	n.d.	385/2294
BbkF	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	21/131	20/243	18/185	9/178	31/201	55/430
	14.07.04	118/354	n.d.	53/284	94/282	n.d.	n.d.
	08.09.04	-/1052	-/2421	39/464	-/456	n.d.	n.d.
	16.11.04	29/223	23/304	34/208	25/187	n.d.	24/441
BaP	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	111/697	102/1221	94/980	48/930	159/1029	155/1207
	14.07.04	255/764	n.d.	211/634	214/643	n.d.	n.d.
	08.09.04	-/442	-/730	58/685	-/690	n.d.	n.d.
	16.11.04	48/372	31/409	59/363	39/291	n.d.	32/575
DahA	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	23/146	29/342	20/212	10/201	35/225	56/436
	14.07.04	47/245	n.d.	31/172	27/176	n.d.	n.d.
	08.09.04	-/62	-/98	2/21	-/38	n.d.	n.d.
	16.11.04	3/26	4/49	4/27	4/28	n.d.	4/67
BghiP	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	27/169	28/330	22/229	12/225	41/264	80/618
	14.07.04	129/386	n.d.	59/320	98/295	n.d.	n.d.
	08.09.04	-/215	-/465	7/80	-/129	n.d.	n.d.
	16.11.04	19/145	16/209	22/134	16/123	n.d.	22/400
INDE	11.02.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	24.03.04	11/67	11/136	9/98	5/94	17/107	38/292
	14.07.04	27/139	n.d.	23/125	18/105	n.d.	n.d.
	08.09.04	-/152	-/243	4/49	-/84	n.d.	n.d.
	16.11.04	8/59	7/93	10/64	7/54	n.d.	13/230

In Table 73 the mean PAH content differences between the inlet and the outlet, their standard deviations, their minima and their maxima are shown. The greatest differences were observed for phenanthrene, pyrene, chrysene and benz[*a*]anthracene. Almost no changes were observed for acenaphthylene and the six ring compounds

Table 73: Differences [ng L^{-1}] between inlet and outlet samples taken in March, July, September and November in Dover, Calais and the Channel. Shown are the mean, the standard deviation and the minimum and maximum values.

[ng l^{-1}]	mean	std	min	max
ATHY	5	4	-6	9

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ATHE	24	14	0	41
FLRE	129	24	97	175
PHEN	1128	218	805	1278
ANTH	28	13	11	37
FLUA	170	57	101	210
PYR	392	94	203	452
BaA	253	190	-17	113
CHRY	361	120	108	476
BbkF	55	33	12	36
BaP	126	43	52	199
DahA	18	15	0	38
BghiP	41	10	28	46
INDE	17	5	12	24

Origin of PAHS

To determine the origin of the PAHs and to compare all samples again a plot of the isomeric ratios of phenanthrene/anthracene and fluoranthene/pyrene is used. It can be seen that all outlet samples clearly showa petrogenic character, whereas the remaining samples cannot clearly be assigned to one specific source. Only the samples taken in November are all characterized by low phenanthrene/anthracene ratios and only two samples show comparable ratios to the outlet samples: Dov 4 (July) and D 350 (September). As the samples taken from points C5 and D5 directly in front of the seawater scrubber outlet do not show such a pattern it is most probable that Dov 4 and D350 were not influenced by the seawater scrubber and that these ratios, even though they are similar, do not relate to a PAH input from the “Pride of Kent”.

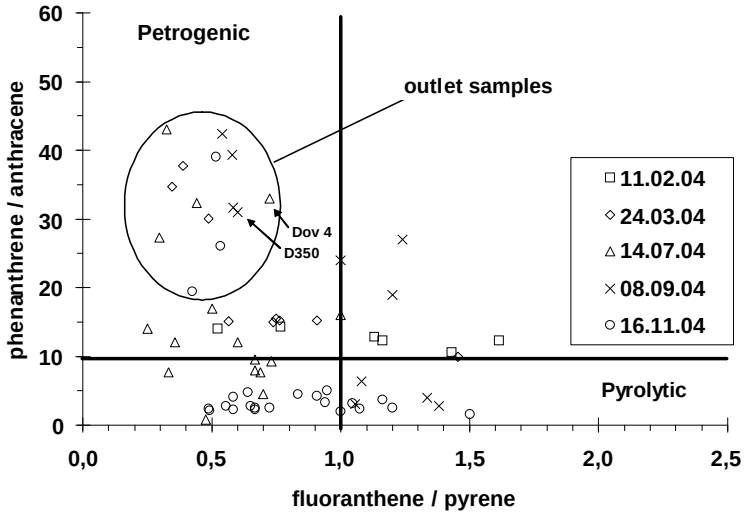

Fig. 60: Isomeric ratios of Phe/Anth vs. Flu/Pyr for all sampling dates.

For a further classification of the harbour samples a principal component analysis was performed including all samples taken inside the ports of Dover and Calais and from the inlet of the seawater scrubber. The results are shown in Table 74 and Fig. 61. Both eigenvectors together make up 72.4 % of the total variance within the samples. For eigenvector 1 the values are all within the same order of magnitude and therefore the samples are separated according to their distribution along the x-axis. The November and the March samples all have positive x-value while the September and July

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samples are all located on the left part of the diagram. These samples also show only a low variability in eigenvector 2. They are all situated in a range of ± 1, whereas the March samples show negative and the November samples positive y-values. From Table 74 it can be seen that eigenvector 2 is positive especially for chrysene, benz[*a*]anthracene and benzo[*b*]fluoranthene plus benzo[*k*]fluoranthene while it is negative for fluorene, phenanthrene, dibenz[*a,h*]anthracene, benzo[*ghi*]perylene and indeno(1,2,3,*c*,*d*)pyrene. The lower the y-value for the specific sample is the more the samples contains of the latter compounds and the higher the y-value the more the more they contain of the first group of compounds. Therefore the samples taken in November contained more chrysene and benz[*a*]anthracene whereas the samples taken in March contained more phenanthrene and more high molecular weight compounds. As in March the heating period was still going on the water was enriched in high molecular weight PAHs whereas in November the heating period just started and therefore the pyrolytic influence was not as strong.

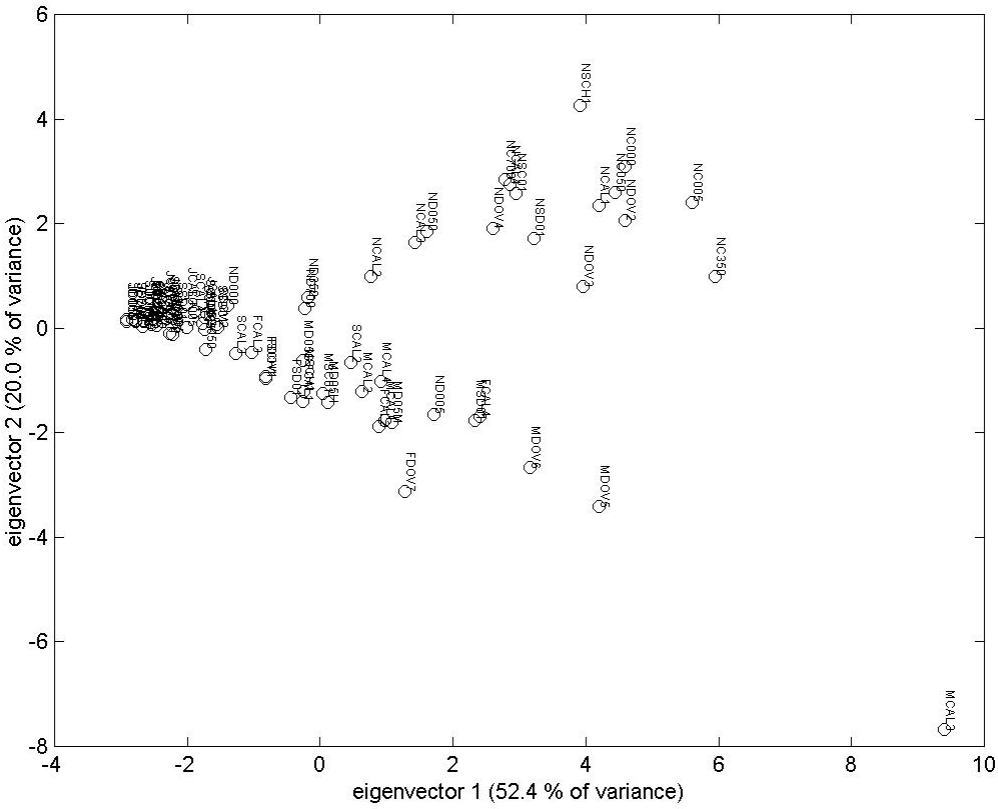

Fig. 61: Results of the PCA of all harbour samples taken in February (F), March (M), July (J), November (N) and September (S)

Table 74: Feature vector for the PCA of all harbour samples taken in February, March, July, November and September

	52.4 % (14.0)	20.0 % (14.0)
acenaphthylene	0.28	0.14
acenaphthene	0.20	0.18

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fluorene	0.27	-0.26
phenanthrene	0.21	-0.38
anthracene	0.30	0.03
fluoranthene	0.32	-0.05
pyrene	0.31	0.02
benz[*a*]anthracene	0.27	0.36
chrysene	0.29	0.32
benzo[*b*]fluoranthene + benzo[*k*]fluoranthene	0.31	0.28
benzo[*a*]pyrene	0.33	0.06
dibenz[*a,h*]anthracene	0.15	-0.38
benzo[*ghi*]perylene	0.23	-0.36
indeno(*1,2,3,c,d*)pyrene	0.21	-0.38

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8.6.4 Plankton samples

In March all samples with the exception of point Cal 3 (Calais: Quai de la Loire) were dominated by diatoms. Most of them were single cells, but colonies were also observed. The sample from point Cal 3 was dominated centric diatoms (*Coscinodiscus* sp.). During these sampling the samples were only analysed qualitatively. During the sampling in July, September and November plankton cells were counted quantitatively and concentrations were calculated as cells per mL. The results are shown in Table 75.

Table 75: Results of plankton cell counting. Concentrations are given in cells per mL.

	July C 5	July C700	July D 5	July D700	Sept. C 5	Sept. C700	Sept. D 5	Sept. D700	Nov. C 5	Nov. C700	Nov. D 5	Nov. D700
water volume [mL]	2900	2880	2595	2950	3390	3440	3290	3390	5000	4950	4370	4550
concentrated volume [mL]	71	58	63	53	51	59	55	56	50	50	50	47
examined volume [mL]	5	5	5	5	5	1	5	5	1,0	1	1	1
examined fields	30	30	30	30	25	30	30	30	50	40	50	50
Amphora							8					
Anomoneoneis								0	1	4		
Biddulphia	3	5		1	8	8	1	3			1	1
Chaetocerus	3								7	10		
Coscinodiscus	0	1	1	3	6	30		1	13	22	5	5
Ditylum	1			1	1				2			2
Eucampia					3	63			10	18		
Gymnodiunium									1	4		
Gyrodinium									2			
Lauderia									16	62		
Melosira	5				6	38			58	79	20	31
Metromonas										1		
Navicula			1			3		1	2	2	1	
Nitzschia	12	10	8	6	53	165		3	7	13		19
Olotrychales									50			
Peridium					1							
Pleurosigma		1	2	1	1	3	2	1				
Porosira										1		
Rhaphoneis				2	12	16	1	1	2	2		
Rhizosolenia	2	4	3	1	6	3		1	25	69	1	1
Schroederella										5		
Scenedesmus										8		
Skeletonema		5										
Stauroneis		1										1
Tetraedron						19		3				
Tetraselmis											1	
Thallasionema				13	5	14			2	15		
Thallasiosira	6			1	4	5				1		
Triceratium	1					5		1				
Ulothrix					32	25	9		50			
Calanoid					1			1		1		
Polychaeten Larve				1								
Sum	34	25	14	27	136	398	20	13	247	316	30	59

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The highest cell contents were determined for sample C 700 taken in September, but also for the samples taken at points C 5 and C 700 in November. The samples taken in Calais contained more cells than those taken in Dover. This may be the result of the higher nutrient concentrations measured inside the port of Calais. Because of its enclosed architecture, this harbour becomes more easily eutrophicated and therefore more plankton can potentially grow. In all samples diatoms were dominating. The species observed the most often was *Nitzschia spec.* Zooplanktan like copepods were only detected rarely.

As no plankton data from the past are available for the ports it cannot be said whether the observed plankton contents were higher or lower than in the past. Even when the concentrations were different from those in the years before a direct influence of the seawater scrubber cannot be assumed *a priori* as the variability can also be due to natural reasons like weather, nutrient availability and predation. The potential effect of the SWS can, however, be theoretically estimated. The samples taken in July, September and November contained more dissolved inorganic nitrogen (DIN) in the outlet water than the inlet water (Table 76). The greatest difference was observed for the sample taken in Dover in November. Marine organic material of phytoplankton origin has a specific ratio of different elements. This is termed the Redfield ratio and describes the (C, N, P, O, H)-composition as $C_{106}H_{263}O_{110}N_{16}P_1$. It can be assumed that C, H, O and P are not production limiting as C, N, O and H are ubiquitous and P was found in all samples in sufficiently high concentrations. Thus, the phytoplankton growth only depends on the concentrations of inorganic N-compounds.

Nevertheles, the calculations presented in the following must remain highly speculative as e.g. no data on overall water exchange rates are available. In addition, the volume of the water body into which the cooling water disperses during one stay in the port is not known. Similarly the short-term variability of nutrients over the investigation period is unknown as is the variability in light.

One mole of a Redfield molecule weighs 3550 g and contains 224 g N. One mole N weighs 14 g. Taking the highest DIN difference from Table 76 and assuming that all DIN added from the SWS is converted to biomass, than 9.59 µmol L^{-1} would produce 2.13 mg biomass L^{-1}. Due to the large in-port and seasonal variations it is difficult to relate this value to actual ambient DIN values. Taking 10 µmol L^{-1} as low and 60 µmol L^{-1} as high ambient concentrations then from these 2.2 and 13.3 mg biomass L^{-1}, respectively, could be produced.

This calculation does, however, not take into account duration of input or mixing processes. During one hour the seawater scrubber/cooling system produces 70 t of outlet water. Normally the „Pride of Kent“ stays 45 minutes inside the harbour and therefore approximately 52.5 m³ or 525,000 L effluent pass the cooling system. The additional DIN from the SWS/cooling system would thus produce 1.12 kg planktonic biomass during each visit. With five vists of the “Pride of Kent” per day this would a total of 5.59 kg additional biomass/d.

Assuming that the volume affected by the discharge of 52.5 m³ SWS/cooling water is 6,000 m³ (area 20 * 50 m area to a depth of 6 m), then this relates to a volume dilution of 114. At the same time, in the 6000 m³ 5.04 kg biomass could be produced from ambient 10 µmol DIN L^{-1}. A dilution of the 1.12 kg

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biomass produced from the excess DIN added (see above) by a factor 114 gives 9.77 * 10^{-3} kg. Thus even at the lowest ambient DIN concentrations an effect of the SWS nitrogen input is negligible.

The port of Dover has a total water volume of 2.538 km³.

Table 76: DIN differences between inlet and outlet samples taken in Dover, Calais and the Channel.

[µmol L^{-1}]	Jul.	Sep.	Nov.
Dover	5,82	5,40	9,59
Channel	1,50	-0,36	3,45
Calais	3,79	0,91	5,48

8.7 Results of mussel analysis

During the last sampling (November) mussels were taken from the quay wall at point C0. These mussels were analysed for to their PAH contamination to have the possibility to compare the results of the accumulation test. Also there is more literature available that deals with PAH in mussels than with seawater contents. The results of the analyses are presented in Table 77 and are arranged according to mussel size. It can be seen that the highest total concentration (all 16 EPA PAHs without naphthalene) was determined in the largest size class (40-50 mm). In this class the dominating compounds were phenanthrene, acenaphthylene, fluoranthene and pyrene. Within the medium size class (30-40 mm) the major compounds were fluoranthene, chrysene and benz[*a*]anthracene. In the smallest size class (20-30 mm) the same order was observed. Dibenz[a,h]anthracene and indeno(1,2,3,*c*,*d*)pyrene were not detected. The differences in the PAH concentrations might have two reasons. The larger the mussels are, the older they are. These mussels have lived for a longer time in contaminated water and therefore had a longer time to accumulate contaminants. Another reason might be the metabolic rates of the mussels. As these organisms were taken from the littoral (zone influenced from tides) they are not as large as mussels taken from the sublittoral. The mussels in the size class 40-50 mm are therefore relatively old and the older and the bigger they are, the more energy is needed for metabolic processes and the less energy can be used for gamete production. As this production is the major indirect process for the mussel to reduce lipid-soluble pollutants the pollutants become enriched in the older mussels.

Table 77: PAH concentrations [ng g^{-1}] measured in mussels taken from the quay walls at sampling point C0 and Bio Concentration Factors (BCF).

size class [mm]	20-30	30-40	40-50	20-30	30-40	40-50
mean size [mm]	25.7	34.8	43.1	BCF	BCF	BCF
ATHY	-	10	231	-	1.4	31.4
ATHE	5	8	43	0.4	0.6	3.4
FLRE	11	28	154	0.8	2.0	10.9
PHEN	50	58	343	2.0	2.4	14.0
ANTH	4	8	65	0.3	0.6	5.0
FLUA	83	89	178	8.4	9.0	17.9
PYR	58	65	173	11.7	13.1	34.8
BaA	60	70	110	6.9	8.1	12.7
CHRY	75	84	121	7.1	8.0	11.5
BbkF	23	25	33	-	-	-

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BaP	14	15	36	-	-	-
DahA	-	-	-	-	-	-
BghiP	4	3	14	-	-	-
INDE	-	-	3	-	-	-
sum	389	462	1505	3.7	4.4	14.3

This increase can also be seen in the Bio Concentration Factors (BCFs, Table 77). BCFs are calculated as the quotient of the concentration observed in the mussel and the concentration measured in the water. If the BCF is 1 there is no bioaccumulation of the observed pollutant. If the BCF is smaller than one, the organism uses regulatory processes to reduce its pollutant concentration. Higher concentrations reflect that no such processes are available or that these processes work inefficiently only. Mussels are organisms that have very few possibilities to reduce their pollutant contents. That is why they are often used in monitoring studies. In Table 77 it can be seen that the mussels of the size classes 20-30 mm and 30-40 mm show similar BCFs whereas the BCFs in the bigger mussels are higher. This supports the explanations given before.

In the literature several biomonitoring studies employing mussels are available. In South Shetland mussels Webster et al (1997) determined phenanthrene concentrations comparable to those measured in Calais but Flua, Pyr, BaA and Chry concentrations one order of magnitude lower. In the southern Baltic mussels contained total PAH amounts (Σ EPA) between 8.6 and 29.2 ng g^{-1} (Potrykus et al 2003). As these samples were taken at sites away from anthropogenic influence the mussels have lower contamination levels whereas Stella et al. (2002) determined PAH concentrations in Italian mussels comparable to those observed in the size classes 20-30 mm and 30- 40 mm.

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8.8 Results of sediment analysis

Sediment samples were taken during the samplings in July, September and November. During all samplings attempts were made to obtain samples from points C5, D5, C700 and D700. Due to currents and due to the state of the bottom surface this was not always possible with the van Veen grab. Therefore samples were obtained at the points shown in Table 78. The sediment samples were taken to clarify whether the composition of the PAHs measured in the water samples at point C5 or D5 is identical with the PAH composition of the sediment. If so an increase in the PAH water concentration might be the result of resuspended sediment, because sediments are generally higher polluted than water samples. Another reason for taking the sediment samples was to check whether the composition of the sediment taken at points C5 and D5 is the same as observed at point C700 and D700. This could give information about the influence of the shipping activities on the sediment, i.e. is the impact is higher at the positions where the ships are berthing or is the contaminated water spreading over the whole harbour before the polluted particles settle down. In the latter case the content and the composition should be similar at both points. If this is the case it can be expected that the effluent water of the seawater scrubber gets highly diluted and the influence onto the harbour would be smaller.

Table 78: PAH concentrations determined for sediment samples taken in July, September and November

date	Jul.	Jul.	Nov.	Jul.	Sep.	Nov.	Jul.	Sep.	Nov.	Sep.
point	Cal 1	C 5	C 5	C 700	C 700	C 700	D 5	D 5	D 5	D 700
ATHY	-	-	-	-	-	-	-	-	-	-
ATHE	15	3	993	2	-	11	15	3	10	2
FLRE	21	7	790	3	7	11	18	6	11	6
PHEN	173	81	8805	20	20	60	102	34	61	38
ANTH	45	18	1177	6	2	15	36	8	20	7
FLUA	564	248	9763	46	16	104	182	114	209	186
PYR	378	170	6948	30	12	70	135	88	166	146
BaA	171	80	5487	25	8	56	107	54	104	73
CHRY	79	26	2562	11	4	22	36	23	40	30
BbkF	138	28	2676	26	6	52	92	28	63	37
BaP	180	42	4520	34	8	72	147	33	94	52
DahA	41	6	702	5	2	10	17	7	15	10
BghiP	123	20	2044	22	8	50	89	27	62	36
INDE	169	24	2272	29	4	55	96	29	69	35
Sum	2098	754	48737	259	97	588	1071	453	925	657

From Table 78 it can be seen that the sediment PAH contents measured at point C5 in November were significantly higher than those measured at the remaining points. A reason for this cannot be given. Perhaps the sample was contaminated with tar or oil. Taking a look at the remaining stations it can be seen that at point Cal 1 higher concentrations were found than at the remaining points. This sample was taken from the harbour wall at a point where there is no berthing activity and where the currents are very slow. This allows fine particles to settle down. As fine particles have a greater

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surface than coarse ones, more PAHs can adsorb to them. At point C 700 the total PAH load was different during the three samplings, with highest contents measured in November and lowest measured in September. This partially corresponds to the water contents which were also highest in November. In Dover at point D5 the lowest overall concentration was also measured in September and the highest in November. The September sample taken form the harbour entrance was higher contaminated than the one taken at the berth. So far no clear trend is visible but it seems that in Dover there is no difference between samples taken at the berth or at the port entrance, whereas in Calais the berth samples seem to be higher contaminated. This would also underline the observations made before. Dover with its relatively open structure and the faster water exchange allows pollutants to be transported over a longer distance, whereas in Calais with its enclosed structure the PAHs mainly remain close to the point where they were released.

From Table 79 it can be seen that the relative PAH compositions are comparable. Only the sample taken in July at point C5 shows in relation to the other samples a higher pyrene and benz[*a*]anthracene value.

Table 79: PAH composition of the sediment samples taken in Calais and Dover in July, September and November in percent.

date	Jul.	Jul.	Nov.	Jul.	Sep.	Nov.	Jul.	Sep.	Nov.	Sep.
point	Cal 1	C 5	C 5	C 700	C 700	C 700	D 5	D 5	D 5	D 700
ATHE	0	0	0	0	0	0	0	0	0	0
FLRE	1	0	2	1	0	2	1	1	1	0
PHEN	1	1	2	1	7	2	2	1	1	1
ANTH	8	11	18	8	21	10	10	8	7	6
FLUA	2	2	2	2	2	3	3	2	2	1
PYR	27	33	20	18	16	18	17	25	23	28
BaA	18	23	14	12	13	12	13	19	18	22
CHRY	8	11	11	10	9	10	10	12	11	11
BbkF	4	4	5	4	4	4	3	5	4	5
BaP	7	4	5	10	6	9	9	6	7	6
DahA	9	6	9	13	8	12	14	7	10	8
BghiP	2	1	1	2	2	2	2	2	2	1
INDE	6	3	4	8	8	9	8	6	7	5

Plotting the isomeric ratios of PHEN/ANTH against FLUA/PYR it can be seen that in all sediments with exception of C700 the PAH composition indicates a pyrolytic origin. In contrary to the sediment, the composition of the PAHs in the water samples often did not clearly indicate the source. This difference might be the result of the faster degradation of PAHs originating from petrogenic sources (see Introduction). Therefore mainly PAHs from pyrolytic processes enter the sediment.

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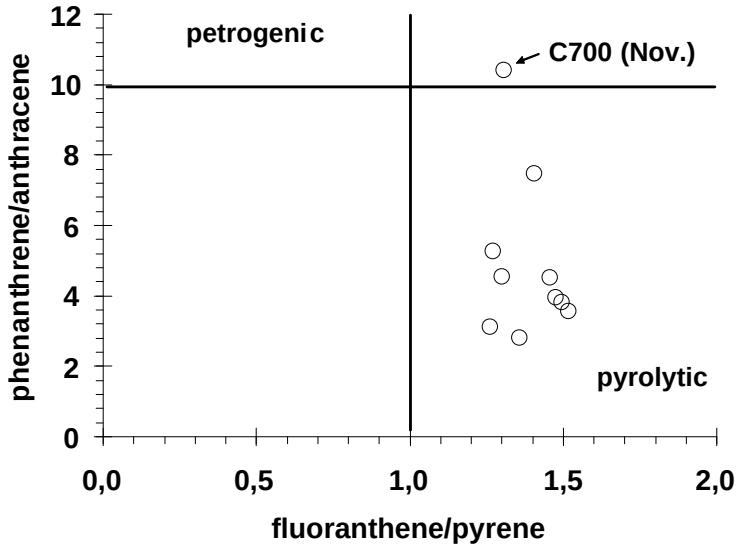

Fig. 62: Plot of isomeric phenanthrene/anthracene and fluoranthene/pyrene ratios of all sediment samples taken in Dover and Calais in July, September and November.

To compare the sediment samples, the water samples and the mussel samples taken in Dover and Calais a principal component analysis was performed. The results are shown in Table 80 and Fig. 63. Eigenvector 1 was responsible for 47.6 % and eigenvector 2 for 18.2 % of the total variance. Eigenvector 1 was mainly positive for the high molecular weight and negative for the low molecular weight PAHs. Eigenvector 2 refers mainly to chrysene, benz[*a*]anthracene and the sum of benz[*b*]fluoranthene and benz[*b*]fluoranthene. These compounds are partially soluble in water. The PCA plot shows that all sediment samples had high values for eigenvector 1 and therefore they show a higher content of high molecular weight PAHs. As this indicates a pyrolytic origin as observed in the plot of the isomeric ratios it can be assumed that the sediment samples were mainly influenced from atmospheric input. The samples of the small and medium sized mussels were taken close to stations C5 and C0. The water samples taken in July are situated at the bottom of the graph whereas the samples taken in November are situated at the top of the graph. This shows that the four and five ring compounds make up a lower percentage of the total concentration in the July samples than in November. In Fig. 63 it can also be seen that the water samples even those taken close to the “Pride of Kent” do not show a PAH pattern similar to the sediment samples. This shows that the sediment which was resuspended by the ship screws does not influence the water samples.

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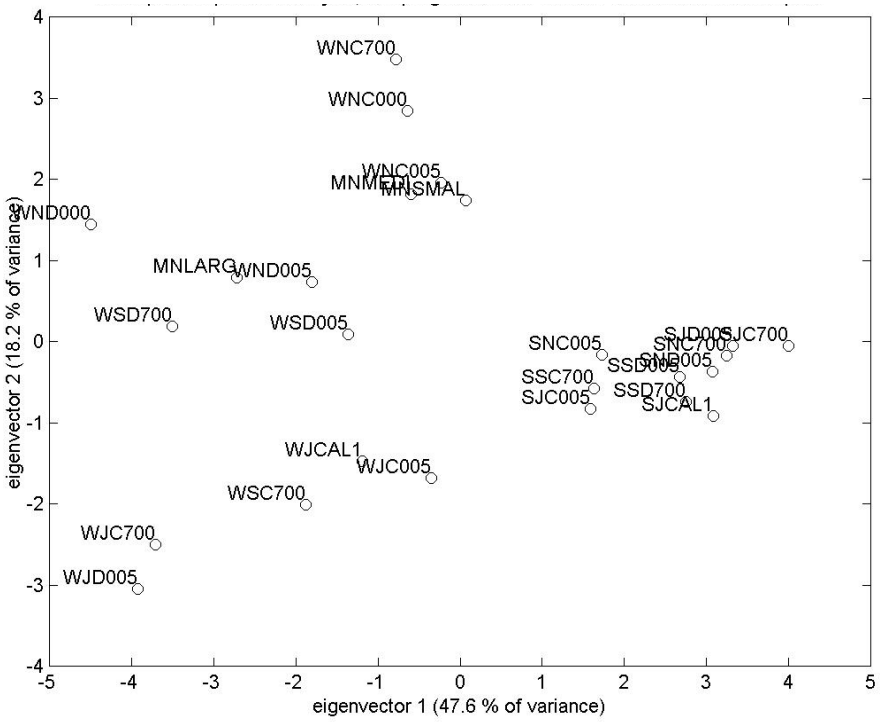

Fig. 63: Principal component analysis of the relative PAH concentrations (percentages) of the water, sediment and mussel samples taken in Dover and Calais in July, September and November. First letter: W=water sample, S=sediment sample, M=mussel sample (SMAL=small 20-30mm, MEDI=medium 30-40mm, LARG=large 40-50 mm). Second letter: J=July, S=September, N=November. Last four letters: sampling point.

Table 80: Feature vector for the PCA of the water, sediment and mussel samples taken in Dover and Calais in July, September and November

compound	EV1	EV2
ATHY	-0.16	0.16
ATHE	-0.30	-0.08
FLRE	-0.34	-0.00
PHEN	-0.30	-0.30
ANTH	-0.11	0.25
FLUA	0.25	-0.13
PYR	0.12	-0.31
BaA	0.15	0.54
CHRY	-0.10	0.55
BbkF	0.33	0.24
BaP	0.35	0.07
DahA	0.34	-0.13
BghiP	0.33	-0.13
INDE	0.33	-0.10

Soclo et al (2000) examined sediments in a French harbour (Cotonou). Here the total PAH content, with a comparable PAH composition to that one analysed in this project, had a maximum value of 1411 ng g^{-1}. Inside the harbours of Rotterdam and Amsterdam (The) sediments were analysed by de Boer et al. (2001). In this case the total contents of about 4000 ng g^{-1} were higher than in Calais.

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9 Results and discussion of the toxicity and accumulation tests

9.1 Lumistox test

The results of the Lumistox test are shown in Fig. 64. For this experiment three independent inlet and outlet samples were taken at points SCH1 and SCH2. All three samples were tested twice for their overall toxicity. The pH values of the outlet and inlet samples are shown in Fig. 64. The inlet samples all had a pH of 8.07. The basic luminescence measured at the beginning of the first test (pH 6.86) was 3478 that one of the second test (pH 7.02 and pH 6.84) was 4206. The figure shows the differences in inhibition between inlet and outlet water. These determined against a 3 % NaCl solution control. Due to the nutrients in the natural seawater which are missing in the NaCl solution also negative values for the luminescence inhibition were determined. It can be seen that all results and also the results plus the determined variance were below 20 % inhibition. As these values were obtained with undiluted samples these results represent the highest values which can be expected. Therefore there is no possibility to calculate the EC_{20} (effective concentration where 20 % luminescence inhibition is observed) and the samples can be regarded as non-toxic. As the Lumistox test corresponds to microbial toxicity it can be said that the effluent of the seawater scrubber has no determinable negative effect on the microbial system of the harbours.

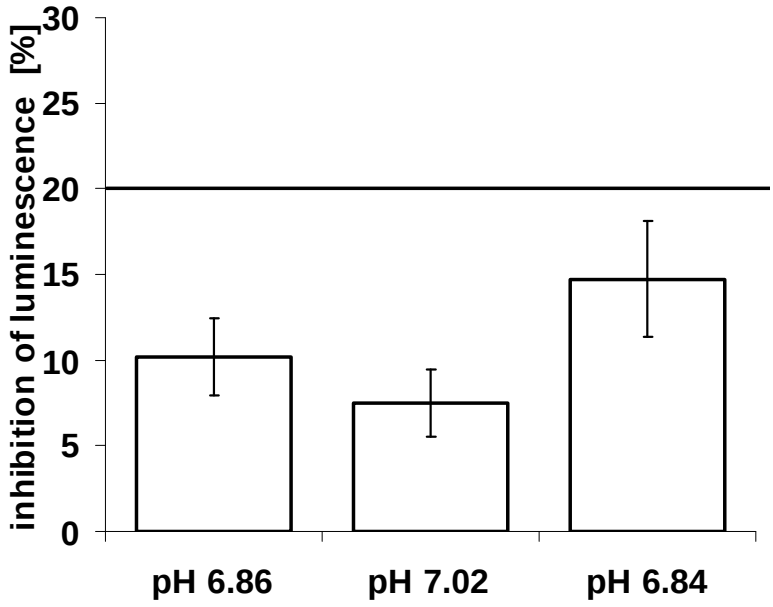

Fig. 64: Results of Lumistox test. Shown are the differences between seawater scrubber inlet and outlet water taken during the sampling in September. The pH shown was the pH of the outlet sample

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9.2 Brine shrimp test

Table 81 and Table 82 show the results of the acute and the chronic toxicity determined with the brine shrimp test. The results for the test performed with juvenile *Artemia salina* are shown in Table 81 those for the test with adults are shown in Table 82. The pH of the outlet water varied between 6.83 and 7.07, that of the inlet water between 8.12 and 8.15. The samples taken for the brine shrimp test were independent from those taken for the Lumistox test. For the test with the juvenile *Artemia* between 34 and 75 individuals and for the adult test 22 to 35 individuals were randomly chosen and put in petri dishes. As can be seen no adult or juvenile *Artemia salina* died during the test, neither after 6 h nor after 24 h. Therefore no toxicity of the outlet water towards *A. salina* could be observed. As the test was performed over a time span of 24 h also no chronic toxicity could be observed. *A. salina* is regarded as key representative for plankton organisms. Therefore it can be stated that the seawater scrubber effluent has no negative effects on plankton organisms.

Table 81: Results of the brine shrimp test performed with 24 h old juvenile *Artemia salina*

juveniles		30 min		6 h		24 h	
	pH	alive	dead	alive	dead	alive	dead
inlet Probe 1	8,13	34	0	34	0	34	0
inlet Probe 2	8,12	37	0	37	0	37	0
inlet Probe 3	8,15	62	0	62	0	62	0
outlet Probe 1	7,07	67	0	67	0	67	0
outlet Probe 2	6,87	75	0	75	0	75	0
outlet Probe 3	6,83	68	0	68	0	68	0

Table 82: Results of the brine shrimp test performed with 4 weeks old juvenile *Artemia salina*

adult		30 min		6 h		24 h	
	pH	alive	dead	alive	dead	alive	dead
inlet Probe 1	8,13	23	0	23	0	23	0
inlet Probe 2	8,12	22	0	22	0	22	0
inlet Probe 3	8,15	27	0	27	0	27	0
outlet Probe 1	7,07	27	0	27	0	27	0
outlet Probe 2	6,87	24	0	24	0	24	0
outlet Probe 3	6,83	35	0	35	0	35	0

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9.3 Accumulation test

9.3.1 Mussel analyses: size, weight, condition index, fat content

In this chapter the results of the combined accumulation and toxicity test, performed with the mussel *Mytilus edulis*, are presented. In Fig. 65 the proportions of the dry tissue, the shell weight and the water content are shown. The sizes of the single mussels are shown in Table 83. “Control 2” contained in comparison to “control 5” and “control 8” more individuals greater than 60 mm whereas in “control 5” and “control 8” there were more individuals smaller than 50 mm. The water content and the dry tissue weight of the latter two are with 26.9 %, 27.2 % and 4.5 %, 5.1%, respectively, higher than in “control 2” with 23.7 % water content and 3.2 % dry tissue weight. A similar behaviour can be observed for the tests “part 01”, “part 04” and “part 07”. In test “part 01” 11 mussels were greater than or equal 60 mm, in “part 04” only 4 and in “part 07” none of the mussels was greater than 60 mm. For the tests “diss 03”, “diss 06” and “diss 09” the size distributions were similar to those of the particulate trial and the controls, with relatively more long mussels in trial “diss 03” and fewer in trial “diss 06” and “diss 09”. In this case the observed relations of water, shell and dry tissue weight are only reflected in the water content. On the right side of Fig. 65 the mean percentages of the water content, the dry tissue and the shell weight of all size classes, are given. It can be seen that increasing mussel size is paralleled by an increase in shell weight and a decrease in relative water content.

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Table 83: length [mm] of all mussels employed for the accumulation test. The colours separate the table in the main classes used for the PAH determination. The first class smaller than 50 mm and the second class between 50 mm and 60 mm

control external basin	part 01	cont 02	diss 03	part 04	cont 05	diss 06	part 07	cont 08	diss 09
15.2	36.2	36.1	31.1	40.2	41.8	35.6	40.1	38.8	43.4
15.8	38.4	36.1	36.8	41.7	44.8	42.5	42.9	41.4	43.7
22.4	39.4	36.7	38.9	42.2	45	43.3	44	41.8	46.7
24.7	40.1	38.2	40.8	43.2	45.4	43.4	44	42.7	49.1
28.2	41	39.3	43.8	43.8	46	43.9	44.1	43.7	49.2
33	44.8	47.8	46.9	43.9	46.4	44.1	45.6	45.5	49.9
33.3	45.8	47.8	49.2	44.7	46.7	44.5	45.6	46.1	50.3
39.1	51.5	49.5	50.4	45.7	47.2	46.1	46.1	46.4	50.9
45.3	52	53.2	52.9	46.1	47.4	46.5	46.3	47.2	52.1
45.3	53.5	53.4	53.3	46.3	47.8	47.3	47.4	47.6	52.8
46.4	54.1	54.9	53.9	47.2	47.9	47.4	47.8	47.8	53
47.1	54.5	55.1	54.1	48.8	48.3	48.2	49.5	48.7	53.2
47.6	55.8	56	55.9	50.1	48.4	48.2	49.6	48.8	53.3
48.2	56.5	56.5	57.1	50.3	48.6	48.6	49.6	49	54.2
48.4	57.5	56.7	58	50.8	49.2	49	50.2	49.7	54.4
49.8	57.6	57.2	58.5	51.4	49.2	49.2	51.2	49.7	55
50	59.8	58.2	59.2	51.6	49.2	49.2	51.3	49.8	55.3
50.2	59.9	58.5	61.1	52.4	50	49.9	51.7	50.4	56.3
50.3	60	59	61.3	52.7	50.7	50.7	52.1	50.7	56.7
50.8	60.1	59.1	61.3	55.2	51.5	51	52.3	51.8	56.8
51.6	61.2	59.2	61.5	55.2	52.1	51.5	52.5	52.3	57
52.6	61.2	59.9	61.7	55.7	52.6	51.6	52.8	52.8	57.7
52.6	62	60.1	62.1	55.8	53.7	51.7	53.4	53.3	58.7
52.6	63.5	61.5	62.8	59.7	54.5	52.5	53.4	53.8	59.1
53.2	66	62	63	59.8	55.8	52.7	53.5	55.1	59.4
53.6	66.5	65.8	63.8	59.9	55.9	53.3	50	55.8	59.9
53.8	67.5	66.8	63.9	60.5	56.1	53.8	54.9	56.6	60.6
54.7	69.7	67.7	64.3	62.5	56.2	54.8	57.1	56.9	61
56.3	70.2	69.6		63	59.4	56.3	59	60.8	62.2
56.5				68.9	70	56.7		62.8	
56.6									
56.8									
57.7									
58.4									
62.8									
64									
70.7									

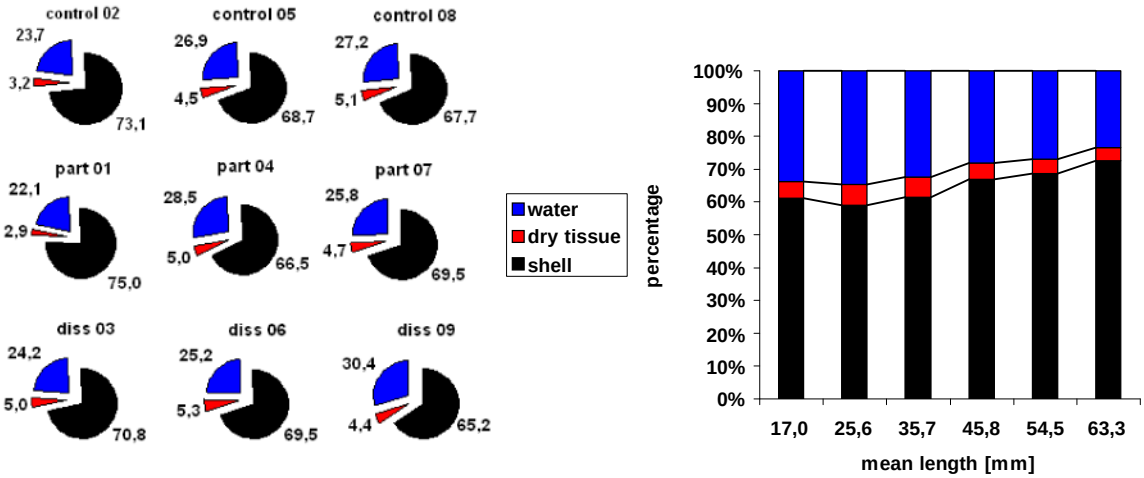

Fig. 65: Mean percentages of shell, dry and wet tissue weight for all mussels used in the accumulation test. Left: percentages for each test, right: mean for all tests.

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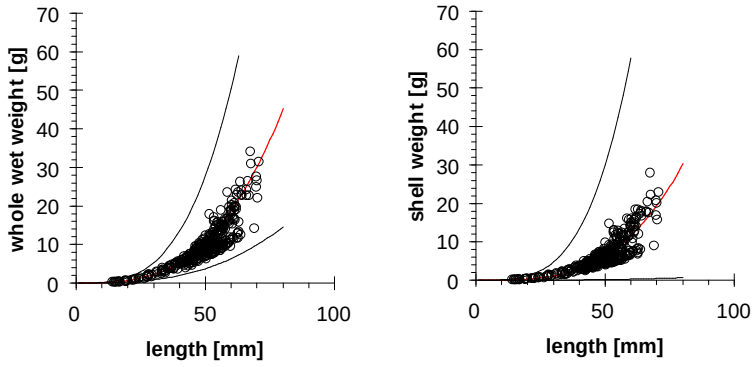

Fig. 66: Correlation plots. Left: whole wet weight against length. Right: shell weight against length. In both cases the red line shows the nonlinear model and the black lines the 95 % confidence interval

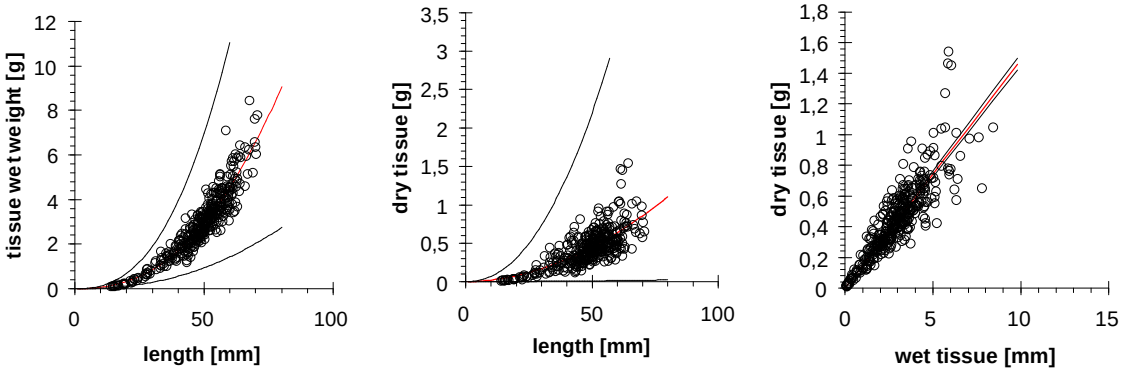

Fig. 67: Correlation plots: Left: wet tissue weight against length. Middle: dry tissue weight against length. Right: dry tissue weight against wet tissue weight. In both cases the red line shows the nonlinear model and the black lines the 95 % confidence interval

In Fig. 66 and Fig. 67 the correlation plots of total wet weight, shell weight, dry tissue weight, and wet tissue weight against shell length and dry tissue against wet tissue weight are shown. The used model functions, their parameters, the 95 % confidence intervals of the parameters and the correlation coefficient R^2 are shown in Table 84. It can be seen that the dependencies between length and shell weight, wet weight and total weight show good correlations, whereas the scatter of the dry tissue weight is much higher.

Table 84: Results of linear and nonlinear regression

dependent variable	weight total [g]	weight shell [g]	weight wet tissue [g]	weight dry tissue [g]	weight dry tissue [g]
independent variable	length [mm]	length [mm]	length [mm]	length [mm]	weight dry tissue [g]
function	$y = a \cdot x^b$	$y = a \cdot x^b$	$y = a \cdot x^b$	$y = a \cdot x^b$	$y = a \cdot x$
Parameter a	6.732E-05	1.206E-05	2.332E-04	2.564E-04	0.1488
min 95 %	4.700E-05	7.115E-07	1.200E-04	1.490E-05	0.1450
max 95 %	8.800E-05	2.341E-05	3.465E-04	4.980E-04	0.1530
Parameter b	3.062	3.363	2.412	1.910	
min 95 %	2.886	3.131	2.291	1.675	
max 95 %	3.238	3.595	2.533	2.145	
R^2	0.826	0.767	0.874	0.551	0.753

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9.3.2 Mussel analyses: PAH content, accumulation, mortality

In Fig. 68 the results of the standardized mussel tissue extraction and the R^2 values for the calibration lines are shown. The error bars for the mussel tissue are the errors given by the manufacturer. The error bars of the determined values are calculated by aid of the GC-MS accuracy according to the values given in Table 17 (25 µg l^{-1}). It can be seen that all values were determined within the given error range and accuracy with the exception of fluorene. In this case the determined concentration was 11.3 ± 0.2 ng g^{-1} whereas the given value was 10.2 ± 0.4 ng g^{-1}. It has to be considered, that only the accuracy of the GC-MS measurement was stated and not the accuracy of the whole method, which would be somewhat higher. For the mussel extraction the accuracy of the method was not determined like for the extraction of the water samples, because a standardised reference material as control was available.

All determined PAH concentrations are shown in Table 85. The compounds added permanently during the test are indicated in italics. The contents of these compounds are also visualised in Fig. 69. The "background" concentrations of those compounds that were not added during the test are shown in Fig. 70. These contents can be regarded as negative control. In the latter graph it can be seen that acenaphthylene, acenaphthene and dibenz[*a,h*]anthracene are equally concentrated in all mussels, benzo[*a*]pyrene, benzo[*ghi*]perylene and indeno(1,2,3,*c,d*)pyrene are slightly increased and fluorene, benz[*a*]anthracene and benzo[*b*]fluoranthene plus benzo[*k*]fluoranthene are nearly doubled in the controls from the external basin. It can also be seen that within the external controls the PAH contents are slightly increased in those mussels greater than 50 mm. For the mussels used in the test an inverse distribution was observed. In most cases the concentration is lower in the mussels smaller than 50 mm. Fig. 69 also shows a quite similar distribution of PAHs in the controls from the external basin and from the controls in the test. The PAH concentrations of those compounds added permanently are increased clearly in the mussels from the particulate and the dissolved test in comparison to the controls and those mussels from the external basin. Comparing the results from the dissolved and the particulate test there is no difference recognizable. To check this observation statistically, a t-test was performed. The test was performed in two different ways: I) to check whether there is a significant difference between the two size classes and II) to check whether there is a significant difference between the dissolved and the particulate tests. The used test was the t-test for testing the equality of the variances of two dependent random samples and was calculated according to

$$t = s_1^2 - s_2^2 \cdot \frac{n-2}{4 \cdot s_1^2 \cdot s_2^2 \cdot \left(1 - R^2\right)}$$

where s_1 and s_2 are the standard deviations of two samples, n is the number of compared rows and R^2 is the correlation coefficient. The reference value can be taken from a significance chart (degrees of freedom = 8, α = 5 %; $t_{(8/0.05)}$ = 2.31). In both cases the calculated t-value was below 2.31, therefore it can be said that the observed differences in variability are coincidental. A measure for the correlation can be given by the R^2 which is 0.9763 for the comparison of the PAH concentrations in the mussels

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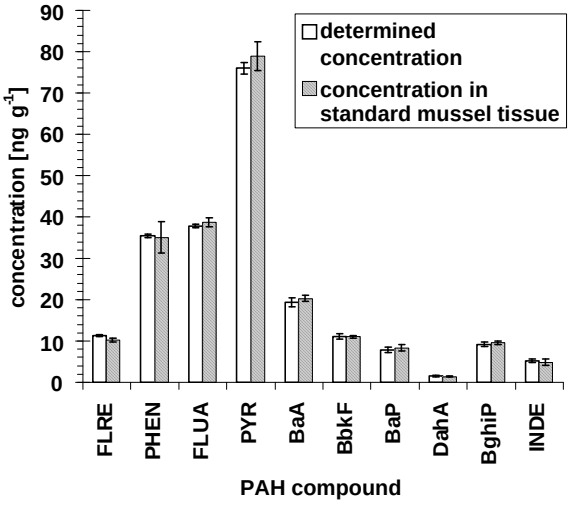
smaller and greater than 50 mm, and 0.9877 for the comparison of the PAH concentrations in the mussels from the dissolved and the particulate test. This shows a high correlation between the results.



compound	steepness	section	R^2
naphthalene	0,0046	-0,0045	0,9998
acenaphthylene	0,0035	-0,0034	0,9988
acenaphthene	0,0024	-0,0027	0,9987
acenaphthene-D10	0,0025	-0,0027	0,9995
fluoren	0,0027	-0,0027	0,9981
phenanthrene-D10	0,0041	-0,0043	0,9985
phenanthrene	0,0046	0,0000	0,9974
anthracene	0,0033	-0,0047	0,9947
fluoranthene	0,0043	0,0008	0,9905
pyrene	0,0043	0,0000	0,9895
benz[a]anthracene	0,0044	0,0000	0,9990
chrysene-D12	0,0044	0,0000	0,9979
chrysene	0,0044	0,0197	0,9962
benzo[b]fluoranthene + benzo[k]fluoranthene	0,0067	-0,0047	0,9988
benzo[a]pyrene	0,0025	-0,0028	0,9987
perylen-D12	0,0026	-0,0042	0,9978
dibenz[a,h]anthracene	0,0019	0,0000	0,9938
benzo[ghi]perylene	0,0030	-0,0037	0,9978
indeno(1,2,3,c,d)pyrene	0,0024	-0,0029	0,9963

Fig. 68: Left: Comparison of PAH concentrations determined in the standard mussel tissue and the original concentrations. Right: correlation coefficients, steepness and section of the external reference lines

Table 85: PAH concentrations [ng g^{-1}] determined for the mussels in the accumulation test. Compounds indicated in italics are those added daily. ext are the mussels taken from the external basin, 02, 05 and 08 are the controls, 03, 06 and 09 are the mussels from the dissolved test and 01, 04 and 07 are the mussels from the particulate test.

test	length	ATHY	ATHE	FLRE	*PHEN*	*ANTH*	*FLUA*	*PYR*	BaA	*CHRY*	BbkF	BaP	DahA	BghiP	INDE
ext	< 50	3	5	31	*92*	*23*	*218*	*152*	17	*7*	16	9	1	10	9
ext	> 50	3	4	27	*106*	*32*	*223*	*159*	20	*10*	19	10	3	11	10
02	< 50	3	4	8	*45*	*16*	*119*	*223*	7	*1*	10	8	0	10	9
02	> 50	3	4	8	*39*	*12*	*69*	*171*	9	*1*	10	7	2	8	7
05	< 50	2	4	24	*65*	*16*	*99*	*195*	6	*0*	10	6	0	9	6
05	> 50	3	4	26	*84*	*27*	*124*	*219*	7	*0*	7	6	1	7	5
08	< 50	3	4	7	*46*	*16*	*84*	*160*	5	*0*	11	8	0	8	7
08	> 50	3	5	11	*61*	*21*	*116*	*226*	5	*0*	8	6	0	8	6
03	< 50	3	4	6	*612*	*460*	*1218*	*851*	6	*219*	9	7	0	8	7
03	> 50	3	4	7	*594*	*434*	*1171*	*846*	6	*199*	10	8	1	10	8
06	< 50	3	3	19	*786*	*619*	*1759*	*1186*	6	*299*	8	6	1	7	5
06	> 50	3	4	9	*833*	*286*	*1729*	*1115*	7	*214*	5	4	0	6	4
09	< 50	3	4	16	*267*	*162*	*641*	*484*	11	*214*	15	10	4	13	10
09	> 50	3	3	6	*271*	*147*	*782*	*587*	7	*207*	11	6	0	8	6
01	< 50	3	4	7	*430*	*297*	*1141*	*818*	9	*254*	10	7	0	8	8
01	> 50	3	4	7	*393*	*231*	*1039*	*764*	8	*214*	10	7	0	8	7
04	< 50	3	4	7	*591*	*308*	*1205*	*861*	6	*270*	12	7	0	9	7
04	> 50	2	4	29	*709*	*437*	*1168*	*832*	7	*162*	10	7	2	9	7
07	< 50	3	3	19	*478*	*317*	*985*	*710*	5	*205*	10	7	0	8	7
07	> 50	3	3	6	*665*	*247*	*1354*	*916*	6	*211*	7	5	0	7	5

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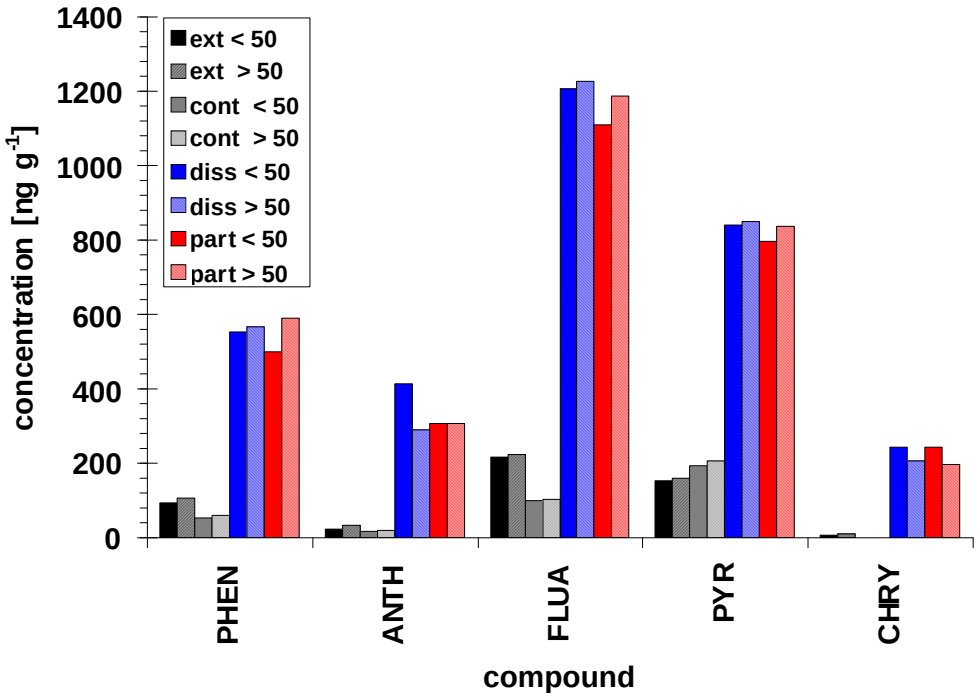

Fig. 69: Mean concentrations of the added PAHs, determined for the different accumulation tests.

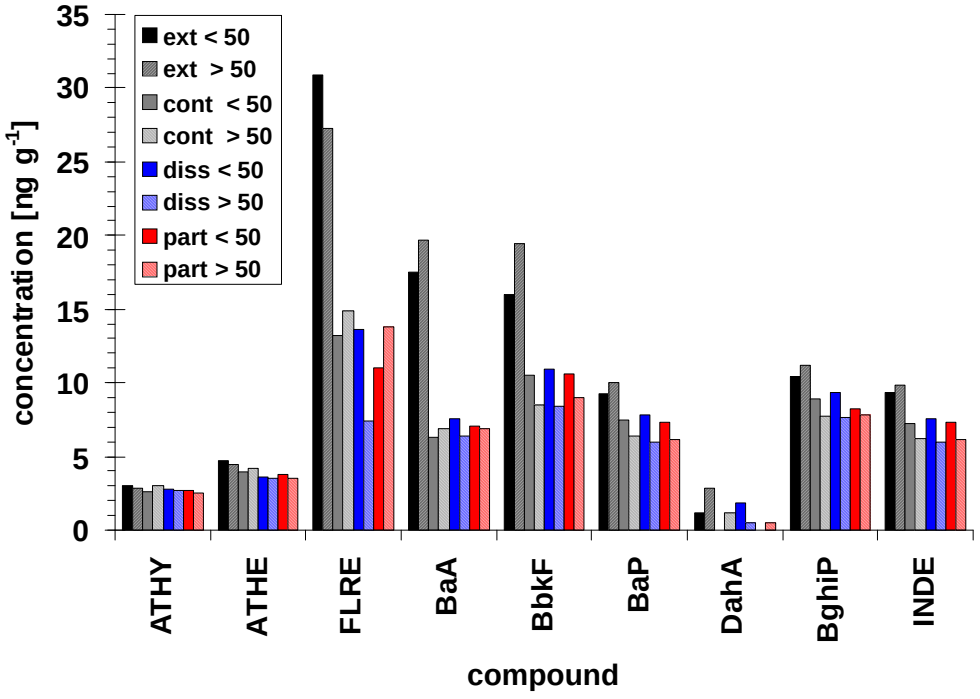

Fig. 70: Mean concentrations of the PAHs which were not added during the test, determined for the different accumulation tests.

Table 86: expected PAH concentrations in the mussels if all added PAHs would have been accumulated

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		PHEN	ANTH	FLUA	PYR	CHRY
particulate 01	<50	47926	20036	18668	8141	1399
	>50	47926	20036	18668	8141	1399
particulate 04	<50	47652	19921	18561	8095	1391
	>50	47652	19921	18561	8095	1391
particulate 07	<50	47199	19731	18385	8018	1378
	>50	47199	19731	18385	8018	1378
diss 03	<50	35501	14841	13828	6031	1037
	>50	35501	14841	13828	6031	1037
diss 06	<50	43475	18175	16934	7385	1269
	>50	43475	18175	16934	7385	1269
diss 09	<50	53405	22326	20802	9072	1559
	>50	53405	22326	20802	9072	1559

Table 87: Percentage of accumulated PAHs, calculated as quotient of expected and observed PAH contents in the mussels.

		PHEN	ANTH	FLUA	PYR	CHRY
particulate 01	<50	0.9	1.5	6.1	10.0	18.2
	>50	0.8	1.2	5.6	9.4	15.3
particulate 04	<50	1.2	1.5	6.5	10.6	19.4
	>50	1.5	2.2	6.3	10.3	11.6
particulate 07	<50	1.0	1.6	5.4	8.9	14.9
	>50	1.4	1.3	7.4	11.4	15.3
diss 03	<50	1.7	3.1	8.8	14.1	21.1
	>50	1.7	2.9	8.5	14.0	19.2
diss 06	<50	1.9	1.6	10.2	15.1	16.8
	>50	1.9	1.6	10.2	15.1	16.8
diss 09	<50	0.5	0.7	3.8	6.5	13.2
	>50	0.5	0.7	3.8	6.5	13.2

During the whole test (30 days) the mussels in the dissolved and particulate trials were fed with the following absolute PAH amounts:

- phenanthrene = 640475 ng
- anthracene = 267750 ng
- fluoranthene = 249475 ng
- pyrene = 108800 ng
- chrysene = 18700 ng

Y

If the mussels would have accumulated the total amount of the added PAHs the concentration shown in Table 86 would have to be expected. The values were calculated as the quotients of the total amount of the PAH compounds and the sum of the dry tissue weight of all mussels used in the concerning test. Comparing these values with the actually determined compound concentrations, the accumulation rate can be calculated, as quotient of the observed concentration and the expected concentration in percent. The results are shown in

Table 87. It can be seen that from the added phenanthrene 0.5 % to 1.9 %, the anthracene 0.7 % to 3.1 %, fluoranthene 3.8 % to 10.2 %, the pyrene 6.5 % to 10.6 % and the chrysene 11.6 % to 21.1 % were accumulated.

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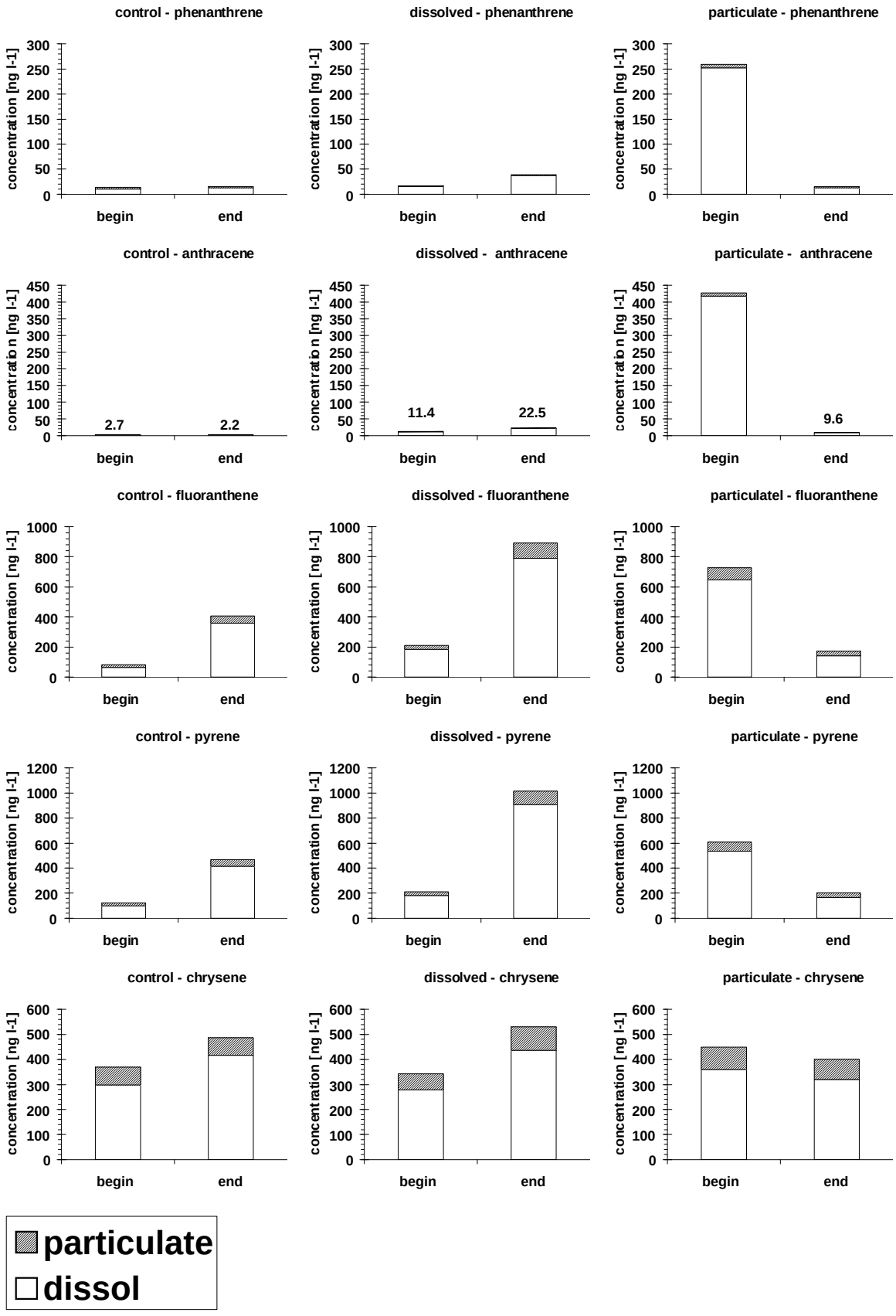

Fig. 71: Concentrations of phenanthrene, anthracene, fluoranthene, pyrene and chrysene [ng l^{-1}] measured in the aquaria of the controls, the particulate and the dissolved test one hour after a water exchange and right before the following water exchange (3 days). Contents are separated into dissolved and particulate fractions.

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During the accumulation test the contents of the added PAH compounds phenanthrene, anthracene, fluoranthene, pyrene and chrysene in the water of the aquarium were determined half an hour after a water exchange and directly before the following water exchange after three days. The results are shown in Fig. 71. The pH, salinity and the water temperature are shown in Table 88. Within the water samples of the controls the phenanthrene and anthracene contents were equally low in the beginning and at the end of the three day period whereas the pyrene, chrysene and fluoranthene increased during that time. The same was observed in the samples from the aquaria of the dissolved test. Also the contents were quite similar. In contrary to the increase of dissolved pyrene, chrysene, and fluoranthene, the contents observed in the particulate test showed another distribution: the phenanthrene content in the beginning was 259 ng l^{-1} and in the end 15 ng l^{-1}, the anthracene contents were 427 ng l^{-1} and 10 ng l^{-1} the fluoranthene contents 727 ng l^{-1} and 174 ng $l^{-1,}$ the pyrene contetnts 609 ng l^{-1} and 203 ng l^{-1} and the chrysene contents 448 ng l^{-1} and 400 ng l^{-1}, respectively. The observed differences between the PAH contents of the particulate and the dissolved tests and the increase of fluoranthene cannot be explained. One reason might be that the water of the aquarium was not mixed thoroughly enough before taking the samples. This was difficult as stirring was not possible because of the mussels in the aquarium. This would also explain why mainly dissolved PAHs were determined whereas the particulate PAH fraction was low. The reason for the latter aspect could also be that the samples were not taken directly after the PAH addition, but about half an hour later. As blue mussels are able to filter about 1 l seawater per hour and 30 mussels were inside the aquarium half an hour would be sufficient to filter the whole water volume of 17 l.

Table 88: pH, salinity and temperature determined in the aquariums during the test

	pH	Sal	Temp [°C]
1	7.91	31.5	18.5
2	8.06	31.5	18.5
3	7.83	31.5	18.5
4	7.92	31.5	18.3
5	8.01	31.5	18.5
6	7.94	31.5	18.4
7	7.94	31.5	18.5
8	8.02	31.5	18.5
9	7.93	31.5	18.5

From Table 77 where the PAH concentrations determined for the mussels taken in Calais are shown. It can be seen that the total amount of the mussels smaller than 40 mm in Calais is about the same as those concentrations observed in the external basin and the controls, but the composition is different. The mussels taken in Calais contain higher concentrations of phenanthrene and fluoranthene whereas the mussel taken from the Jade Bay show higher concentrations of high molecular weight PAHs. Due to their life history the mussels are not directly comparable concerning to their PAH concentrations. The mussels in Calais were growing inside an enclosed harbour with high shipping activities. The PAH composition of this harbour has been discussed before. The mussels taken from the Jade Bay were mainly influenced from PAHs reaching them through the atmosphere. Therefore they contain mainly high molecular weight PAHs.

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Although the PAH compositions of the mussels cannot be compared directly, the accumulation rates will be similar. The „Pride of Kent“ discharges about 52.5 m³ of mixed colling water/seawater scrubber effluents during each visit (see 8.6.4 on page 100) in the ports of Dover and Calais, 5 times a day. During one day 252.5 m³ of outlet water would be introduced into each port. Taking the mean PAH differences of Table 73 this would sum up to a total PAH introduction and to a concentration increase of the values shown in Table 89. As only the water volume of the port of Dover was available this calculation was exemplary carroied out with this volume (2.538 km²). In this calculation losses due to biological or chemical degradation (UV, micro organisms, translocation processes) and physical processes (currents, adsorption and settling) are not included. Assuming that one mussel filters about 1 l seawater per hour and using the dry weight calculated according to Table 84 and a mean accumulation rate from

Table 87 then the contents given in Table 90 would be the result after one year of accumulation for one mussel. As inside a harbour there is not only one mussel and as the accumulated PAHs would have to be subtracted from the available PAHs in the water body the real value makes up only a very small fraction of the values in shown in Table 90.

Table 89: Total PAH amounts [mg] that will be theoretically introduced during one day into the ports of Dover and Calais and theoretical concentration increase [pg l^{-1}]

	total amount [mg] released in 1 day	concentration increase [pg l^{-1}] per day
ATHY	1	1
ATHE	6	3
FLRE	34	13
PHEN	296	117
ANTH	7	3
FLUA	45	18
PYR	103	41
BaA	66	26
CHRY	95	37
BbkF	15	6
BaP	33	13
DahA	5	2
BghiP	11	4
INDE	4	2

Table 90: Mean accumulation rate, total accumulation per day and year and resulting contamination after one year for a 20 mm mussel.

mean acc rate [%]	accumulation per day [pg]	accumulation per year [ng]	concentration in a 20 mm mussel after 1 year [ng g^{-1}]
1.3	35	12.8	163
1.7	1	0.4	5
6.9	29	10.6	136
11.0	107	39.1	499
16.3	102	37.2	475

Mortality

This test was also performed as a toxicity test. Therefore the mortality of the mussels was also observed. During the whole test 4 of the 270 employed mussels died. Two mussels of the aquarium “diss 3” after three and after 21 days, one of test “part 7” after seven days and one in aquarium “part 1” after 10 days. As the mussels of the particulate and the dissolved test were equally contaminated with PAHs this mortality can be assumed for all mussels in the tests. Four mussels of the 180 mussels

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died, this gives a mortality of 2.2 %. When the tests are considered separately than the mortalities in the particulate test would be 3.3 %, 0 % and 3.3 %. For the dissolved tests the result would be 6.6 %, 0 % and 0 %. These values are within the natural variability. Therefore it can be stated that the PAHs had no toxic effect on the mussels. As this test was performed over a time span of 30 days it can also be stated that the PAH composition of the effluent has no chronic toxic effect on the mussels.

To check the constitution of the mussels, the fat and the shell index (SI) were determined. The results are given in Table 91. The higher the fat content and the higher the SI is, the better the conditions of the mussels were. It can be seen that the SI for the mussels taken in Calais was about double the SI determined for the mussels used in the test. The reason for this might be that the mussels for the test were stored in the external basin where no additional food than the seston and plankton collected together with the mussels was available. The mussels of Calais were collected directly inside the harbour. Harbours are characterized by eutrophication and high bioproduction and therefore enough food for the mussels was available.

Low fat and SI values were only determined for “part 1”. In this test the mean shell length was 55.4 mm whereas in the remaining particulate tests the shell length was shorter. Bigger mussels need more food and therefore they faster suffer starvation. This could also be a reason why some of the mussels died during the test.

Table 91: Mean shell index and fat content determined for the mussels of the accumulation test and for the mussels taken in Calais

test	SI	fat content [%]
Calais	13.1	n.d.
ext basin	7.4	2.2
cont 2	5.0	5.6
cont 5	6.8	6.1
cont 8	7.7	5.3
part 1	4.4	3.3
part 4	7.6	3.4
part 7	6.9	5.9
diss 3	7.6	3.9
diss 6	7.5	5.9
diss 9	6.9	5.9

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10 Conclusions

During this project the environmental impact of a seawater scrubber has been analysed for the harbours of Calais and Dover. Five sampling campaigns were organised during which samples were taken inside the ports, from the seawater scrubber system and within a transect leading 700 m away from the seawater scrubber outlet. The seawater scrubber, the so-called “Ecosilencer”, was installed in the funnel of the channel ferry “Pride of Kent” to reduce her SO_x emissions. As seawater scrubbing is a wet fluegas desulphurisation process not only SO_x is dissolved but also NO_x, volatile organic compounds, and hydrochloric acid. The dissolved SO_x and NO_x form sulphuric and nitric acids and reduce together with the HCl the pH of the scrubbing effluent significantly. The samples taken from the seawater scrubber system partially showed pH values lower than pH 3. Because of the buffering capacity of seawater due to the bicarbonate system the pH increases again after an initial acidification. This could be shown in several experiments. From these it could also be shown that a mixture containing 40 % of seawater acidified to a pH of 4, i.e. comparable to that what happens in a seawater scrubber, only changes its pH about 0.2 units. To reach this equilibrium several hours were needed but the largest changes were observable already a short time after mixing. On board of the „Pride of Kent“ the seawater scrubber effluent was mixed with seawater from the cooling cycle of the vessel. Thus a significant pH increase could be obtained but the pH was still lower in comparison to the inlet and the surrounding waters. The lowest pH measured in the overboard discharge was 6.2. As many organisms are only able to survive when environmental conditions are stable adecrease in pH might be a risk for those organisms. That is why the United States Environmental Protection Agency has passed a guideline concerning the introduction of acids which states that within the initial mixing zone the pH change is not allowed to be higher than 0.2 units. In the case of the Ecosilencer the initial mixing zone is directly in front of the overboard discharge of the „Pride of Kent“. To check whether there is an observable pH change, samples were taken directly in front of the outlet (1 to 5 m distance) and 50 m, 350 and 700 m away from the outlet. In no sample taken at the first point of this transect a pH decrease was observed. In Calais the natural pH variability was much higher than the variability measured in the transect. This shows that the bicarbonate system in the seawater effectively buffers the acids added by the operation of the Ecosilencer.

Additionally to the acidification the dissolved SO_x increases the sulphate concentration in the effluent. The samples taken behind the Ecosilencer showed a sulphate increase between 14.0 and 18.7 %. In fresh water lakes sulphate might be a limiting factor but in sea water sulphate is a common and conservative component. The inlet samples taken in the Channel can be considered as blank sample, because the inlet water was not influenced by the outlet water and in the Channel the water current is high enough so that an influence of the previous passing of the „Pride of Kent“ can be neglected. In these samples sulphate concentrations between 2590 and 2990 ppm were observed. In the outlet samples values between 2600 and 3052 ppm were determined which accounts for an increase of 0.4 to 4.5 %. As the method to determine this concentration already had an error of 6 % a sulphate increase in the outlet samples cannot be stated for sure. Even if there would be a slight increase the

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influence of the seawater scrubber on the sulphate concentrations in the harbours and therefore on the marine environment would be very low. Additionally it has to be mentioned that in Calais a wide range of sulphate concentrations, between 1479 and 2628 ppm, was observed.

Another nutrient that might be influenced by the seawater scrubber is nitrate. It is formed in the scrubbing process when NO_x is dissolved in water. It is an important nutrient in the sea. In the samples taken after the Ecosilencer in the Channel, the nitrate concentrations were about two to thirteen times higher than in the seawater inlet samples. The cleanup processes on board (cyclones and US filter) did not reduce these concentrations. The only reduction was observed after dilution of the effluent water with the cooling water. In the effluent samples the nitrate was only twice the inlet concentration. To determine the influence of this additionally added nitrogen a calculation was made to determine the amount of additional biomass production. This showed that an increase in primary production in a given year would be less than the actual primary production during one sunny day per square metre.

Another indirect influence of the seawater scrubber that has to be considered is that the reduced pH in the effluent influences the solubility of metal ions. To check this, samples were taken from the seawater scrubber system and analysed for their metal contents. The highest values for all samplings were determined for the samples taken from the settling tank and the pipe leading to the settling tank. This water contains the particles filtered from the water by the cyclones. The high concentrations showed that the cyclones effectively remove contaminated particles. The highest metal contents were determined for iron. As iron is the major compound of ship steel this result is not surprising. In the outlet samples beside iron also copper, nickel and lead were found. These were only detected during two samplings and here also in the inlet samples. The copper might originate from ship coatings that contain copper as antifouling biocide while nickel is like iron a compound of ship steel. With respect to the metals it can be said that the seawater scrubbing process itself has no influence on their contents, but that due to the reduced pH metals are leached from the steel, the tubing and the funnel. If the metals are present in particulate form they are filtered out of the water and retained in the settling tank. The sludge is removed separately and therefore no harm on the marine environment is expected.

Another group of compounds that is enriched in the seawater scrubber effluent are polycyclic aromatic hydrocarbons. These are either dissolved or bound to soot particles which are formed during incomplete combustion processes. The low molecular weight PAHs such as the two and three ring compounds are soluble in water whereas the higher molecular weight PAHs with four rings and more are mainly bound to particles. Therefore not all PAHs can be removed from the water with the US filter and the cyclones which remove only particulates. This is the reason why there were still relatively high amounts of PAHs in the outlet samples. However, in front of the seawater scrubber outlet no increased PAH contents could be determined. In Dover high PAH concentrations were most often found close to the middle or in the western part of the port where the water is shallower. At this point the current speeds are lower and therefore pollutants might be enriched. Close to the berth and at the eastern entrance of the harbour low PAH contents were measured most probably originating from North Sea water, which is lower contaminated with PAHs, and is flowing into the port at this point.

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In Calais the PAH contents were mostly equal at all points. Only during the sampling in March very high contents were observed at point Cal 3. Here a total PAH content of 765 ng l^{-1} was measured which was the highest value determined in all harbour samples. This high concentration was the result of an algal bloom occurring at that point. The plankton cells might have enriched the PAHs by different pathways: the PAHs might have adsorbed to the surface of the cells or the organism itself produced the PAHs or took them up and accumulated them that way. This shows that there are also very high natural variations. Seasonal variations were also observed. In summer the concentrations were close to the detection limit and high molecular weight PAHs were not found at any point. In contrary in late fall and early spring the PAH contents were higher. This variability is the result of fossil fuel burning which is increased during the heating period. This is also the reason why in fall higher amounts of high molecular weight PAHs were measured.

To determine the origin of the PAHs and to exclude the seawater scrubber as probable source regression and principle component analyses were performed and different indices based on isomeric ratios were applied. The latter indicated that the PAHs determined in the seawater scrubber samples originated from a petrogenic source. This was surprising because it can be expected that in a funnel only PAHs of pyrolytic origin should occur. The reason could be that the fuel is not completely combusted. The indices calculated for the harbour samples did not clearly differentiate between a pyrolytic or a petrogenic origin possibly due to the different PAH sources that influence the harbour. On one hand there are big cities close to the ports introducing a high amount of PAHs originating from a pyrolytic origin (shipping, car traffic, heating) and on the other hand there are the shipping activities inside the port that introduce PAHs originating from petrogenic sources. With the linear regression and the principle component analyses it could be shown that the composition of the seawater scrubber samples was different from those observed in the harbours. A change of the signal due to the dilution with the cooling water could be rejected because the PAHs in the outlet samples showed the same distribution as those in the system itself. As data on seawater samples are rarely available in the literature sediment and mussel samples were also taken inside the ports of Dover and Calais. The PAH load of the sediments was comparable to concentrations measured in another French harbour and were lower than in the ports with high shipping activities like Rotterdam and Amsterdam. The mussels were higher contaminated than mussels collected at the Shetlands or in the Baltic.

With respect to temperature, nutrients and PAHs, the two ports showed differences. One reason might be the different architecture. In Calais the harbour is enclosed by walls and is made up of three arms. One arm is separated by a flood gate which is only opened during high tide. The city of Calais and local industry are located next to the harbour and therefore the anthropogenic influence is relatively high. A water exchange is only possible through a relatively small entrance in the north-west of the harbour. In contrary the harbour of Dover possesses two entrances, one in the south and one in the west. This enables a higher water exchange and therefore the water remains inside the harbour for a shorter time. This port has no side arms where water can be retained, as the harbour walls are built around a large basin. Due to this architecture the city of Dover touches the port only at the north side. Because of these differences the environmental parameters determined in the ports were also different. In Dover the salinity was higher and the water temperature was lower in the most cases than

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in Calais. Also the phosphate and nitrogen concentrationsn and in most cases also concentrations of polycyclic aromatic hydrocarbons were lower. The nitrate concentrations determined for the two ports showed a distinct seasonal behaviour. In summer low concentrations were measured, whereas in February and November relatively high concentrations were observed. Nitrate is a limiting nutrient for marine organisms and therefore it is depleted in summer when plankton bioproduction is high. In fall and winter organic nitrogen compounds are remineralised and hence the nitrate concentrations increase.

Additionally to the observations inside the ports and board of the „Pride of Kent“, toxicity tests were performed to determine the overall toxicity of the outlet water. The tests covered inhibition of bacterial luminescence, mortality of brine shrimps and accumulation of PAH by blue mussels (*Mytilus edulis*). None of all this tests did reveal an increased toxicity of the effluent, neither acute nor chronic.

Summarizing the results it can be said that in the effluent the pH was decreased by a maximum of two pH units, the sulphate content was slightly increased and the nitrate concentration was doubled. Close to the seawater outlet in the ambient warters no decrease in pH, no higher nitrate or sulphate values, and no increased PAH or metal contents were determined. Also no toxicity towards bacteria, zooplankton or mussels was determined for the outlet samples. Although the PAHs are increased in the outlet water these would have reached the North Sea anyway by atmospheric deposition after release by combustion. In this case the PAH amounts would have been higher as in the seawater scrubber system a part was collected by the cyclones. Improvement of the cylone efficiency would help to minimise the problem of particulate PAH introduction to the marine environment

Additionally it has to be stated that when the seawater scrubber is to be be used in areas with brackish or fresh waters, the effects might be different. Fresh waters have for example less pH buffering capacitiy – unless the water drains a carbonaceous area - and therefore the critical load for acidity might be reached very fast.

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Appendix

Matlab Source Code for Principal component analysis

```
close all;
clear all;

load alle_harbour.txt;
M = alle_harbour;
num_row = size(M,1);
num_col = size(M,2);
fid = fopen('txt_alle_harbour_neu.txt','r');
ind=1;
while feof(fid) == 0
   h(ind) = fscanf(fid,'%c \n',1);
   ind=ind+1;
end
fclose (fid);
stand1 = 1;              %Standardize values by mean and standard deviation
stand2 = 0;              %Standardize values only by mean
cov1   = 0;              %varialbes for the calcualtion of the covariance
cov2   = 0;              %varialbes for the calcualtion of the covariance
for i = 1:num_col
   A1(i) = mean(M(1:num_row,i));
   B1(i) = std(M(1:num_row,i));
end

% Standardize values

if stand1
   for i = 1:num_row
      for j = 1:num_col
      M_std(i,j) = (M(i,j)-A1(j))/B1(j);
      end
   end
end

if stand2
   for i = 1:num_row
      for j = 1:num_col
      M_std(i,j) = M(i,j)-A1(j);
      end
   end
end

% Calculating covariance matrix
for j = 1:num_col
   A2(j) = mean(M_std(1:num_row,j));
end
for j1=1:num_col
   for j2=1:num_col
      for i = 1:num_row
         cov1 = (M_std(i,j1)-A2(j1))*(M_std(i,j2)-A2(j2));
         cov2 = cov2 + cov1;
         cov1 = 0;
      end
      cov(j1,j2) = cov2/(num_row-1);
      cov2=0;
   end
end


% Computing eigenvalues and eigenvectors
[V,D] = eig(cov);
d = eig(cov);
V = V*(-1);

%Finding max eigenvector values
 [VALUE,INDEX] = sort(d);
Index1 = INDEX(num_col);
Value1 = VALUE(num_col);
Index2 = INDEX(num_col-1);
Value2 = VALUE(num_col-1);
if num_col > 3
    Index3 = INDEX(num_col-2);
    Value3 = VALUE(num_col-2);
end
total_var = sum(d);
Val1_var  = (Value1/total_var)*100;
Val2_var  = (Value2/total_var)*100;
Val3_var  = (Value3/total_var)*100;
disp(sprintf ('\n\n\n'))
disp(sprintf ('Value1 (%2.3f) gives account for %2.1f %% of the total variance (%2.1f) ',Value1,Val1_var,total_var))
disp(sprintf ('Value2 (%2.3f) gives account for %2.1f %% of the total variance (%2.1f) ',Value2,Val2_var,total_var))
```


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```
if num_col > 3
   disp(sprintf ('Value3 (%2.3f) gives account for %2.1f %% of the total variance (%2.1f) \n\n\',Value3,Val3_var,total_var))
end

% Creating feature vector
feat_V (1:num_col,1) = V(1:num_col,Index1);
feat_V (1:num_col,2) = V(1:num_col,Index2);
feat_V = feat_V';
disp(sprintf ('The feature vector for deriving the new data set is \n'))
for i = 1:size(feat_V,2)
   disp(sprintf ('\t %2.2f \t%2.2f',-feat_V(1,i), feat_V(2,i)))
end

% Deriving the new data set
M_std=M_std';
Final_Data = feat_V*M_std;
Final_Data = Final_Data';

% plotting final data
x = Final_Data(1:num_row,1);
y = Final_Data(1:num_row,2);
plot(x,y,'ok')
title('Principal component ananlysis, al harbour samples from all samplings')
xlabel(sprintf ('eigenvector 1 (%2.1f %% of variance)',Val1_var))
ylabel(sprintf (' eigenvector 2 (%2.1f %% of variance)',Val2_var))
str_ind=1;
for i=1:size(x,1)
   text(x(i),y(i),h(str_ind:str_ind+4),'HorizontalAlignment','right','VerticalAlignment','bottom','FontSize',6,'Rotation',270)
   str_ind=str_ind+5;
end
```

Systat source code for linear regression analysis

```
REGRESS
use 'D:\ECOSILENCER_DATEN\Daten\Pn5_161104\reg_5\punkte.syd'
PRINT = LONG
MODEL   P02 = P01
ESTIMATE
PLOT P01*P02 / SMOOTH=LINEAR  CONFI=0.9500
```


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