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HCB, PCB, PCDD and PCDF emissions from ships

David Cooper
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Report Summary

Organisation/Organization

IVL Svenska Miljöinstitutet AB
IVL Swedish Environmental Research Institute Ltd.

Adress/address

Box 5302
400 14 Göteborg

Telefonnr/Telephone

031-725 62 00

Projekttitel/Project title

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Rapportförfattare/author

David Cooper

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HCB, PCB, PCDD and PCDF emissions ships

Sammanfattning/Summary

Since current estimates of hexachlorobenzene (HCB), polychlorinated biphenyls (PCB), dioxins (PCDD), and furans (PCDF) from ships are based on a relatively limited and old data set, an update of these emission factors has been outlined as a target towards improved emission inventories. Consequently and as an assignment from the Swedish Environmental Protection Agency (SNV), the Swedish Environmental Research Institute (IVL) has undertaken a comprehensive study focusing on these emissions from three different ships during December 2003 to March 2004. Analyses were performed on 12 exhaust samples, 3 fuel oil samples and 3 lubricating oil samples from a representative selection of diesel engine models, fuel types and during different "real-world" operating conditions.

The measured emissions correspond reasonably well with previous measurements. The data suggests however that previous PCDD/PCDF emission factors are probably too high. As expected the greatest emissions were observed during main engine start-up periods and for engines using heavier fuel oils. Total emissions for 2002, using the revised emission factors, have been calculated based on Swedish sold marine fuels and also for geographical areas of national importance. In terms of their toxic equivalence (WHO-TEQ), the PCDD/PCDF emissions from ships using Swedish fuels are small (0.37 - 0.85 g TEQ) in comparison to recent estimates for the national total (ca. 45 g TEQ). Emissions from other land-based diesel engines (road vehicles, off-road machinery, military vehicles and locomotives) are estimated to contribute a further 0.18-0.42 g TEQ. Similarly HCB and PCB emissions from these sources are small compared to 1995 national emission inventories.

Nyckelord samt ev. anknytning till geografiskt område eller näringsgren /Keywords

Ship emissions, marine diesel engines, HCB, PCB, dioxins, furans

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Box 210 60, 100 31 Stockholm

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Swedish Summary

Tidigare uppskattningar på utsläpp av hexaklorbensen (HCB), polyklorerade bifenyler (PCB), dioxiner (PCDD), och furaner (PCDF) från fartyg har gjorts utifrån en relativt begränsade databas. För att förbättra detta referensunderlag har IVL Svenska Miljöinstitutet på uppdrag av Naturvårdsverket utfört ett omfattande mätprojekt ombord på tre fartyg under perioden december 2003 – mars 2004. 12 avgasprov, 3 bränsleprov och 3 smöroljeprov från ett representrativt urval av marindieslar, bränsletyp och under olika driftsförhållanden analyserades.

De uppmätta emissionerna överenstämmer ganska väl med den tidigare studien förutom att lägre emissionsfaktorer för PCDD/PCDF har uppmätts här. Som väntat föreligger de högsta emmissionerna i samband med uppstart av huvudmaskineriet samt för motorer som körs med tunga tjockoljor. De totala emissionerna för år 2002 har uppskattats med de reviderade emissionsfaktorerna baserad på i Sverige sålda marina bränslen samt geografiska områden av nationella betydelse. Enligt ämnens toxiska ekvivalenter (WHO-TEQ), är PCDD/PCDF-emissioner små från sjöfart med svensk bränslen (0.61 g TEQ) i jämförelse med de totala nationella mängderna (ca 45 g TEQ). Utsläpp från övriga land-baserade dieselfordon (vägfordon, arbetsfordon, militär fordon samt lokomotiv) bidrar ytterligare med ca. 0.30 g TEQ. Utifrån 1995 data för Sveriges total emissioner, är även HCB aoch PCB emissioner från dessa källor mycket små.

1. Introduction

Over the past two decades exhaust emissions from ships have been the subject of increasing attention throughout the industrial world. Real-world emission data, i.e. actual emissions measured during normal service on board ships as oppose to those at engine manufacturers test beds are especially valuable in this context. The first measurement studies focused mostly on uncontrolled, marine diesel engines for propulsion (main engines) and their nitrogen oxides (NO_x), sulphur oxides (SO_2), carbon monoxide (CO), and hydrocarbon (HC) emissions. This led to the attainment of a first emission database (Melhus and Bergh, 1986; Lloyd's Register Engineering Services, 1990; Lloyd's Register Engineering Services, 1991). Although this pioneering work provided the foundation for drafting guidelines on marine emission inventory reporting (EMEP, 2003; IPCC, 1997), further work was required to verify these early findings and extend the database to include other pollutants, operational modes and engine types. Thus in a second phase, attention was turned to particulate matter (PM), heavy metals and some persistent organic pollutants (POP) including polyaromatic hydrocarbons (PAH), hexachlorobenzene (HCB), polychlorinated biphenyls (PCB), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Lloyd's Register Engineering Services, 1993). In turn, other international groups have contributed to consolidate the early emission factor determinations and evaluate the potential of emission abatement techniques (US Coast Guard Headquarters Naval Engineering Division, 1995; Rideout and Meyer, 1997; Götze, 1999; Cooper et al., 1996; Cooper, 2003). Subsequently, two comprehensive marine emission factor reviews have recently been published which provide a solid reference material for estimating exhaust emissions from ships (Cooper and Gustafsson, 2004; European Commission, 2002a). One should note that although numerous inventories, modelling and review applications can be found in the literature regarding marine emissions, they stem unfortunately from only a few studies engaged in the actual field measurements. Thus in some cases, notably for POPs, and emissions from manoeuvring operational phases, the data set can still be considered as uncertain.

Parallel with the progress in characterisation studies, several regulatory bodies both nationally (Swedish Maritime Administration, 1998) and internationally (International Maritime Organisation, 1997; European Commission, 2002b) have addressed ship emissions and restrictive legislation is either enforced or planned. Nevertheless, sea traffic still represents an appreciable emission source and huge quantities of fuel oil are consumed annually at an increasing rate. A recent estimate, based on International Energy Agency sales data, has assigned a world marine fuel consumption as 123,2 Mton of residual oils and 46,7 Mton of marine distillates for the year 2001 (Endresen et al., 2004). Another investigation calculated almost twice this quantity using a bottom-up approach looking at the fuel consumption rates of individual ships and summing for the global fleet (Corbett and Koehler, 2003). Thus even trace quantities of pollutants from marine fuel oils can lead to significant emission volumes relative to other emission sources. Besides heavy metal fuel contaminants, concern is also associated with POP. Chlorinated forms of the latter are especially toxic (Buckeley-Golder et al., 1999). The origin of fuel oil chlorine is however uncertain and speculative. Refineries use quality control measures indicating only trace quantities of total organic chlorides in crude oil of < 3 ppm but contamination from other sources e.g. degreasing agents, solvents, additives may occur further along the process. Organic chlorides have also been implicated in causing corrosive damage to machinery. One of the most important routes leading to PCDD and PCDF formation in combustion systems has been identified as ash-bound metal chlorides, in particular with copper (Wikström et al., 2003). Thus the possibility of an alternative pathway via salt aerosols (sodium chloride) entering with the combustion air cannot entirely be ruled out.

Although a few studies have focused on PAH emissions, shipboard data on chlorinated organic hydrocarbons such as HCB, PCB, PCDD and PCDF are very sparse (Cooper et al., 1996; Lloyd's Register Engineering Services, 1993). Indeed PCDD and PCDF marine emission inventories have up to now been based on only 6 exhaust samples taken in the field. Sampling difficulties on board ships with sensitive glassware and not least relatively high analysis costs have largely prevented additional confirmatory studies being undertaken. International pressure in making commitments to safeguard the environment has however led to several international agreements concerning POP (UNECE, 1998; UNEP, 2001). These obligations have in turn provided the driving force for the Swedish government, via the Swedish Environmental Protection Agency, to identify and quantify all national sources of HCB, PCB and PCDD and PCDF by January 2005. As a part of this work, a review (Kindbom et al., 2004) was recently compiled but sea traffic emissions were not included except as a qualitative remark. In light of this, the Swedish Environmental Protection Agency initiated the present investigation where the central objective was to provide an improved reference material in order to estimate emissions of HCB, PCB, PCDD and PCDF from Swedish and international shipping in geographical areas of national importance. A secondary aim was even to quantify these species in marine fuels and investigate any operational dependence in the emissions.

2. Experimental

2.1. Strategy and measurement ships

The choice of measurement ships was made with the aim of calculating representative emissions for shipping operating around the Swedish coastline. Thus the ships' main engine (ME) and auxiliary engine (AE) type (i.e. engine speed and power output), fuel used, engine age and mode of operation during service route were all factors taken into consideration. Furthermore sampling time and economic constraints weighed heavily i.e. duration of harbour stops, ship route and locality of ports, etc. The eventual publicity that the measurement results may attract meant that some of the invited shipowners were cautious regarding their involvement. For this reason, anonymity was given to all the ships in the study and only the essential technical details representing their machinery could be reproduced in connection with the work. Information regarding ship route, ship-manoeuvring time in the ports, engine model and some engine parameters etc. were classed as restricted. Thus the final ship / engine / fuel combinations used in the study represented a compromise of all these factors (Table 1). The three subsequent measurement campaigns were conducted over the period December 2003 – March 2004.

Table 1. Specifications of the six measurement ships

Ship	A	B	C
Type	Passenger ferry	Transoceanic Container/Ro-Ro	Ro-Ro cargo ship
Measurement region	Baltic Sea	North Sea	Baltic Sea
Year interval of build	10 – 20 years old	10 – 20 years old	< 10 years old
ME type	Medium speed diesel	Slow speed diesel	Medium speed diesel
ME fuel [a]	Low sulphur residual oil (RO)	Residual oil (RO)	Low sulphur residual oil (RO)
AE type	Medium speed diesel	Medium speed diesel	High speed diesel
AE fuel [a]	Marine gas oil (MGO)	Residual oil (RO)	Marine gas oil (MGO)

[a] Fuel analyses given in Table 3.

On board each ship, several different types of samples were collected where analysis priority was given to the exhaust samples (in order to determine the total emissions). Due to budget restrictions, some of the fuel oil and lubrication oil samples taken were therefore not fully analysed. Regarding the exhaust samples, four were taken per ship. Three samples from the ME exhaust were collected consisting of one "start-up" sample and two consecutive samples at "steady state" engine load. Finally, one sample was taken at the AE exhaust also during steady state engine load conditions. The engine loads applied during the measurements were entirely dictated by the operational requirements of the ships under real-world conditions and thus measurements at specific engine load settings (as in standard test cycles) were not undertaken. This meant that some differences between the ships in the load settings were inevitable but generally the steady state ME engine loads were between 50 – 90% of maximum while the AEs were slightly lower at 30 - 70% of maximum. For the start-up samples, differences in engine operation between the ships were much more pronounced. The aim was to sample from the point of engine ignition (cold start) followed by a warm-up period with idling and then with variable loads while the ship manoeuvred out of the harbour. The start-up sample was stopped ca. 10 minutes after a stable steady state engine load was obtained. Thus in practise the start-up sample for some ships could involve a longer manoeuvring period while passing through an archipelago. An additional aspect to consider in this context was the subsequent detection limit in the final analyses (see section 2.4 below).

In order to gain an insight into the possible origin of any organic chlorine species in the fuel, samples of the fuel oil used for each engine tested were collected and also some samples of clean and used lubrication oil. The latter samples were of interest in order to verify previous findings where 10 – 50 times greater chlorine quantities were reported in the clean lubricating oil than the fuel oils (Cooper et al., 1996). All HCB, PCB, PCDD and PCDF analyses (oils and exhaust samples) were undertaken following the European standard method (European Committee for Standardisation, 1996) by an accredited and well renowned laboratory; the Environmental Chemistry group at Umeå University (SWEDAC accreditation number 1808). The Swedish National Testing and Research Institute (SWEDAC accreditation number 1002) carried out other analyses of the fuel oil properties.

2.2. Exhaust sampling location

Sampling locations along the exhaust channels were chosen with regard to obtaining a representative sample and practical considerations i.e. available space for the measurement equipment, ambient temperatures, and safety regulations. The most suitable solution was often to choose a site in the upper engine casing within the funnel housing although locations on the lower decks were also used. In all cases, an adequate number of straight exhaust channel diameters were present upstream (> 5) and downstream (> 2) of the sampling holes, thus reducing error from uneven cross-sectional concentration profiles. Two sample holes with threaded plugs (2” and 2 ½” size) were made in the exhaust channels by the ship’s crew in good time before the measurements.

2.3. Measurement parameters and methodology

Besides the pollutants of primary concern (HCB, PCB, PCDD and PCDF), simultaneous measurements of CO, CO_2 and O_2 were also undertaken in the exhaust.

Unfortunately budget restrictions meant other species of interest such as NO_x, HC, and PM were not included in the project. All measurements were based on international standard procedures where possible (International Organisation of Standardisation, 1996; European Committee for Standardisation, 1996). IVL Swedish Environmental Research Institute employ accredited methods for marine emission measurements of, among other parameters, CO, CO_2 and O_2 (SWEDAC accreditation number 1213).

Some measurements (CO, CO_2, O_2) relied on continual sampling using a continual emission monitoring system (CEMS) with data logged on-line with a computer, while other parameters were based on grab samples (HCB, PCB, PCDD and PCDF) taken over a given time period. In addition to the measurements at the exhaust channel sampling sites, other periodic measurements of general engine parameters (International Maritime Organisation, 1997) were undertaken in the engine control room. An overview of the measurement parameters, methods and instrumentation together with relative uncertainty is presented in Table 2. All specific emissions were calculated via the carbon balance method (i.e. carbon input from the fuel balanced against carbon output in the form of measured CO_2) (International Organisation of Standardisation, 1996). This was reasonably reliable for the steady state samples but the problem with assigning fuel consumption during varying engine loads probably doubled the uncertainty in the emissions for the start-up samples.

Table 2. Measurement parameters, equipment used and relative uncertainty for the steady state exhaust samples (all gas parameters were measured in the dry exhaust gas)

Parameter	Equipment (Analysis method)	Uncertainty
CO, ppm	Maihak Multor 610 gas analyser (infra-red absorption)	± 8% [a]
CO_2, vol-%	Maihak Multor 610 gas analyser (infra-red absorption)	± 6% [a]
O_2, vol-%	Maihak Multor 610 gas analyser (paramagnetic)	± 5% [a]
HCB, ng nm^{-3}	Out of stack filter and absorption on PUF (GC-MS analysis)	± 35% [b]
PCB, ng nm^{-3}	Out of stack filter and absorption on PUF (GC-MS analysis)	± 35% [b]
PCDD/PCDF, ng nm^{-3}	Out of stack filter and absorption on PUF (GC-MS analysis)	± 35% [b]
Exhaust flow, wet nm^3 h^{-1}	Calculation using carbon balance	± 5% [c]
Barometric pressure, kPa	Vaisala analogue barometer model PTB 101B	± 0.1% [c]
Air temperature, °C	Nordtec Testo 600	± 2% [c]
Relative air humidity, %	Nordtec Testo 600	± 2% [c]
Engine load, kW	From ship instrumentation [c]	± 5% [c]
Fuel consumption, g kWh^{-1}	From engine test protocol and corrected for fuel calorific value	± 10% [c]

[a] Accredited method with uncertainty at the 95% confidence interval as defined by the Swedish Board for Technical Accreditation (SWEDAC).

[b] Based on accredited analysis method (for most congeners) with calculated uncertainty as 29% at the 95% confidence interval as defined by SWEDAC. These errors were combined with those from sampling to give an estimated uncertainty.

[c] Estimated error or specified by instrument manufacturers (assumed as one standard deviation or at 68% confidence interval).

2.4. HCB, PCB, PCDD and PCDF measurements

Regarding HCB, PCB, PCDD and PCDF, the exhaust sampling technique chosen was that based on the cooled probe method (variant 1) described in European Committee for Standardisation, 1996. This equipment uses a cooled glass probe, two 2-litre condensate flasks (one containing distilled water spiked with standard and one containing ethylene glycol) followed by a cartridge with polyurethane foam (PUF) adsorbent and particle filter. This sampling equipment choice was recommended by the analysis laboratory based on past experience with samples from land-based combustion facilities in order to guarantee optimum detection limits (1 ng sample^{-1}, 0.1 ng sample^{-1}, 0.05 ng TEQ sample^{-1} for HCB, PCB and PCDD/PCDF respectively). In practise however, the glass sampling train proved too rigid for the present application (excessive vibration) and the high exhaust temperatures (220 – 400 °C) caused difficulties with water cooling along the glass extraction probe in the stainless steel probe housing. Furthermore, the cramped environment at the measurements sites and non-vertical exhaust channels proved to be a significant problem. A modification of the sampling apparatus was therefore necessary. To this end, short pieces of flexible Teflon tubing were used at critical bends along the sampling train and a glycol-cooled condenser equipped with a thermometer was used immediately downstream of the glass extraction probe. The glycol cooling media (ca. 40% solution) was recycled through a portable compressor cooler and circulation pump to maintain cooling of the sample gas (< 20 °C) before passing through the impingers and polyurethane foam adsorbent cartridge.

Traversing along the cross-section of the exhaust channels with the probe during sampling was neglected since it could be assumed that the PM concentrations were uniform in view of the sampling site location (straight exhaust sections) and small PM size (sub-micron particles). The latter also meant that the isokinetic sampling condition could be relaxed if necessary. A further disadvantage with the apparatus that became apparent when sampling, was the use of plane filters. For the fine PM in the diesel exhaust samples, the filter quickly became fully loaded causing a drop in sample flow. Thus for all sampling events, sampling interruption with filter change (up to three times per sample) was necessary. Arguably one could have reduced the total sample volume (and flow) to avoid this but high priority was given to obtaining the best possible detection limits for the samples.

According to the analysis laboratory and method description (European Committee for Standardisation, 1996), the optimum detection limits obtained for the sampling apparatus required sample volumes of 1 – 3 m^3 at flow rates of 0.5 – 2.5 m^3/h. Bearing in mind the importance of minimising detection limits where possible and the available time for the start-up samples, the aim was to collect ca. 1.0 m^3 for these samples and 3.0 m^3 for the steady state samples (which had a more flexible time constraint). In light of the probable PM size distribution, the filter loading problems described above, and also the exhaust flow variations encountered at manoeuvring, strict isokinetic sampling was not possible for the start-up samples. Indeed, for similar reasons, isokinetic sampling was not performed in the previous marine PCDD/PCDF study (Lloyd's Register Engineering Services, 1993; Compaan et al., 1992). Despite this however, the target sample volumes were met for all exhaust samples in the present work except for one of the ME steady state samples on ship C where only 2.0 m^3 was collected due to an impending arrival in port.

HCB, PCB, PCDD and PCDF were analysed using gas chromatography coupled to a mass spectrometer (GC-MS). Unfortunately some minor difficulties arose however, as identified in the laboratory report (Appendix 3). Firstly, due to the relatively low sample concentrations measured, the quality requirement that the blank level should be ten times lower than the sample was not always achieved. In fact for some cases, the blanks were at the same level as the samples. A second problem was in determining some of the PCB species, although this was partly overcome by using an alternative method but at the expense of poorer recovery values of the internal standard. In addition, for a few of the PCB and HCB analyses, interference was encountered which prevented the assignment of a measured value. The oil analyses proved challenging and rather poor recoveries were obtained which increased the uncertainty considerably. Note that added internal standards were used for all samples and the results were not corrected for recovery of the standards.

Rather than using the sum of the different quantities of all congeners, convention is to report PCDD/PCDF emissions (and to a lesser extent PCB) as a measure of their toxicity. Several systems (World Health Organisation WHO, International, Eadon and Nordic) therefore exist for estimating the Toxic Equivalence (TEQ) for the seventeen determined individual congeners of PCDD and PCDF in a sample. For the Eadon system however only twelve species are included. Each congener has an assigned weighting fraction depending on its toxicity. All systems base the highest toxicity (factor = 1) for 2,3,7,8 tetra-chlorodibenzo-p-dioxin but some slight differences occur for the other congeners but these are generally small. For example, the only difference between the WHO and International systems is the assignment for the 1,2,3,7,8 penta-chlorodibenzo-p-dioxin which has a factor of 1 for WHO but 0.5 for the International system. The TEQ convention for reporting means that in some cases large quantities of a certain congener can be determined but the TEQ value can still be very small (i.e. if the congener has a low toxicity). Furthermore, some PCB species are not included in the TEQ conversion. This is the underlying reason why in many cases the total PCB can be significant but the PCB as WHO-TEQ are not. Total PCB in these samples refers to the sum of homologues from tri- to deca-chlorinated PCB species. When faced with results using different TEQ systems, one can usually assume comparability in view of the high measurement uncertainty in the underlying measurements.

Regarding the detection limit (DL) this was defined as a signal from the analysis equipment which corresponded to three times the signal from instrument noise. The DL can vary for different congeners and even for different samples. In the cases where a species was measured as less than the DG, a value of 0.5 x DG was assigned for that species when summing all species to obtain the TEQ.

3. Results and discussion

3.1. Fuel oil and lubrication oil analyses

The main analysis results of the fuel oils and lubrication oils are compiled in Tables 3 and 4 respectively. Speciated PCB, PCDD and PCDF data are presented in Appendix 2. All fuels were supplied in Sweden except for FO1. Note that not all the oil samples taken could be analysed due to budget restrictions. Those analysed were chosen to enable comparisons and contribute to the representativity of the study.

Unfortunately no other data on the contents of HCB, PCB, PCDD and PCDF in marine fuel oils has been found in the literature. Total organic chlorine contents have however previously been determined as; < 2 (gasoil), and, 1.2 and 11 mg/kg for two residual oils (Lloyd's Register Engineering Services, 1993; Compaan et al., 1992). In addition, total chlorine contents were measured for two samples in Cooper et al., 1996, as 0.41 mg/kg (gasoil) and 2.36 mg/kg (residual oil). With a reservation for the poor recoveries and the fact that some analyses are lacking for some fuels, the results tentatively indicate that fuels with higher organic chlorine contents (e.g. ship B's residual oil) are likely to give higher HCB, PCB, PCDD and PCDF exhaust emissions. A similar correlation has also been observed for marine PAH emissions (Cooper, 2003).

Table 3. Fuel oil analysis data

	Ship A (ME) [e]	Ship A (AE) [e]	Ship B (ME and AE) [e]	Ship C (ME) [e]	Ship C (AE) [e]
Type of fuel oil [d]	RO	MGO	RO	RO	MGO
Sample identification	FO3	FO2	FO1	FO5	FO4
Density at 15 °C, g cm^{-3}	0.933	0.884	0.990	0.988	0.851
Viscosity at 50 °C, cSt	176	9.83	405	347	2.89
Net cal. value, MJ kg^{-1}	41.84	42.55	40.11	40.62	42.82
Carbon, % m/m	87.5	86.4	86.7	87.5	86.7
Hydrogen, % m/m	12.3	12.8	10.6	10.5	12.8
Nitrogen, % m/m	0.21	0.06	0.52	0.56	< 0.05
Oxygen, % m/m	< 0.2	0.6	< 0.2	0.6	0.4
Sulphur, % m/m	0.50	0.16	2.2	0.80	0.11
PCDF, µg kg^{-1}	0.006	- [b]	1.5 [a]	- [b]	0.089
PCDD, µg kg^{-1}	0.078	- [b]	0.91 [a]	- [b]	0.10
PCDD/F WHO-TEQ, µg kg^{-1}	0.008	- [b]	0.16 [a]	- [b]	0.011
HCB, µg kg^{-1}	< 0.2	- [b]	< 0.6	- [b]	- [c]
Total PCB, µg kg^{-1}	28	- [b]	12	- [b]	3.2
PCB WHO-TEQ, µg kg^{-1}	0.0003 [a]	- [b]	0.0011	- [b]	0.006 [a]

[a] Note that the recoveries of the internals standard of these samples were poor. The results presented have however been adjusted for these losses but provide only indicative values with an appreciable uncertainty.

[b] Sample taken but not submitted for analysis due to budget limitation.

[c] Evaluation of analysis result was not possible due to interference in chromatogram.

[d] RO = Residual Oil, MGO = Marine Gas Oil (for ship A, the MGO was also classed as a Wide Range Distillate).

[fe]ME = main engine, AE = auxiliary engine.

Regarding the lubrication oil, the analyses indicate levels similar to the fuel oils. It is interesting to point out however that the clean, unused lubricating oil from ship C had higher contents of POP than the dirty lubricating oil. One of the former uses for PCB, before their production ceased in the mid-1980s, was as an additive in various hydraulic, cutting and lubrication oils (Fűll, 2001).

Table 4. Lubrication oil analysis data

	Ship A (ME)	Ship B (ME)	Ship C (ME)	Ship C (AE)
Type	Dirty	Dirty	Dirty	Clean
Sample identification	SO2	SO1	SO4	SO3
PCDF, µg kg^{-1}	- [b]	0.16 [a]	0.025	0.27
PCDD, µg kg^{-1}	- [b]	0.079 [a]	0.10	0.23
PCDD/F WHO-TEQ, µg kg^{-1}	- [b]	0.25 [a]	0.010	0.036
HCB, µg kg^{-1}	- [b]	4.8	< 2.5	< 2.3
Total PCB, µg kg^{-1}	- [b]	9.3	20	22
PCB WHO-TEQ, µg kg^{-1}	- [b]	0.0005	0.0004	0.001

[a] Note that the recoveries of the internals standard of these samples were very poor. The results presented have however been adjusted for these losses but provide only indicative values with an appreciable uncertainty.

[b] Sample taken but not submitted for analysis due to budget limitation.

3.2. Exhaust emissions

For conciseness, a general overview of the average specific emissions determined is presented in Table 5. Following international convention, these emissions refer to the brake power delivered from the engine (and not supplied heat energy). Concentration profiles as a function of time during the separate sampling events are shown in Appendix 1. Emissions of the individual PCB, PCDD and PCDF congeners are compiled in Appendix 2 while the underlying analysis report is presented in Appendix 3 (HCB, PCB, PCDD and PCDF analyses). Fuel-based emissions expressed as ng kg $fuel^{-1}$ can be obtained by dividing the ng kWh^{-1} emission factors given in Table 5 by the fuel consumption in g kWh^{-1} multiplied by 0.001.

Since in some cases the congeners have been reported as less than the detection limit (three times the noise response from the analysis equipment), half of the detection limit has been used to calculate the TEQ value for the sample. As pointed out in section 2.3, caution should be exercised in interpreting the values for engine power, exhaust flow and fuel consumption for the start-up samples which carry an extra uncertainty. One should also note that the results for HCB, PCB, PCDD and PCDF have not been corrected for blank values that in several cases (notably HCB and some PCB congeners) were significant (see section 2.4). In general, most of the analysed PCDD/PCDF values for individual congeners were above the detection limits (with the exception for the samples from ship A and the AE sample from ship C). For the average PCDD/F WHO-TEQ ng $sample^{-1}$quantities found in the samples, these were 1.6 – 2.9 times the corresponding laboratory blank (ship B), and 2.3 – 3.6 times for ship C (ME samples).

The quantities in the blanks were however at the same level as the samples for ship A and the ship C AE sample. For the PCB WHO-TEQ ng sample^{-1}quantities, all samples were above the laboratory blanks 1.3 – 1.7 times (ship A), 2.3 – 3.3 times (ship B), and 2.0 – 6.7 times (ship C). For HCB, sample quantities exceeded blanks by 23 – 55 times (ship B) and 70 – 125 times (ship C ME start-up and AE samples). The remaining samples were below the detection limits and at a level similar to the blanks. Despite the fact that in most cases maximum sample volumes were taken (ca. 3.0 m^3), the detected quantities can be considered as low relative to those in the laboratory blanks. Ideally, laboratory blanks should be 10 times lower than sample quantities. The recoveries of the internal standards determined were in general acceptable for most analyses. There were however some specific exceptions i.e. recoveries < 20% and > 150% (especially for the oil analyses, and several HCB analyses).

As expected, the results indicate a wide range in the emissions between all samples. This is especially so for HCB, where non detectable amounts (< 0.4 ng kWh^{-1}) were measured for the ME on ship C while 500 ng kWh^{-1} was measured for the ME start-up sample on ship B. The agreement for PCDD, PCDF, PCB and HCB obtained between similar samples (e.g. sample pairs 3 and 4, 6 and 7, and, 10 and 11) indicates however a good reproducibility in the measurements (note that sample 4 was taken at a higher engine load than sample 3).

In general, the highest HCB, PCB, PCDD and PCDF emissions have been measured for the ME start-up samples. These conditions are characterised by relatively poor combustion conditions (also high CO emissions). Assuming the PCB, PCDD and PCDF contents in the fuel combined with the specific fuel consumption as input, a rough estimate of the destruction efficiency through the combustion zone of these species can be made. For example consider total PCB and sample 3. One can calculate a PCB input flow with the fuel as 211 x 11630 x 12 x 10^{-9} = 0.029 g/hr (from data in table 3 and 5). Since the output PCB flow in the exhaust is calculated as 200 x 10-9 x 11630 = 0.0023 g/hr (Table 5), then a destruction of 92% of the original PCB in the fuel must occur to complete the mass balance. Similarly, with the other steady state ME samples for ship B, the destruction efficiency can be determined as ca. 93% (PCB) and 99.8% (for PCDD and PCDF). For samples 6 and 7 of Ship A respectively, the corresponding values can be averaged as 99.5% (PCB), 90% (PCDF) and 99% (PCDD). For the AE sample 9 of Ship C, the destruction efficiencies are ca. 80% (PCB) and 99.4% (for PCDD and PCDF). Clearly some caution must be exercised when considering the uncertainties and assumptions in this type of calculation, but the indications are that additional PCB, PCDD and PCDF formation in the combustion zone is unlikely.

Table 5. Summary of the engine operating conditions and the specific exhaust emissions measured (measurement uncertainties are presented in Table 2 except for start-up and manoeuvring samples which are estimated as twice those in Table 2)

Ship / engine	B / AE	B / ME	B / ME	B / ME	A / ME	A / ME	A / ME	A / AE	C / ME	C / ME	C / ME	C / AE
Operation [a]	ss	stm	ss	ss	stm	ss	ss	ss	stm	ss	ss	ss
Fuel type	RO	RO	RO	RO	RO	RO	RO	MGO	RO	RO	RO	MGO
Sample id.	1	2	3	4	5	6	7	8	9	10	11	12
Engine power, kW	1 390	4 010	11 630	18 040	2 570	4 120	3 900	420	490	3 160	3 160	310
Fuel consumption, g kWh^{-1}	213	218	211	211	215	203	203	254	210	195	195	196
Wet exhaust flow nm^3 h^{-1}	9 310	57 810	87 020	127 240	20 120	23 560	22 740	3 630	3 930	18 410	18 680	1 510
CO, ppm	97	514	29	26	176	188	170	95	241	63	59	208
CO, g kWh^{-1}	0.77	9.0	0.26	0.22	1.65	1.27	1.18	0.97	2.35	0.44	0.42	1.18
CO_2, vol-%	5.41	2.53	4.36	5.06	4.68	6.10	5.99	5.00	4.40	5.712	5.63	6.99
O_2, vol-%	15.85	17.61	14.85	14.14	14.25	12.38	12.75	14.64	15.56	13.72	13.87	11.27
PCDF, ng kWh^{-1}	0.8	4.3	1.0	0.6	<0.3	0.2	0.03	0.1	2.0	0.6	1.7	0.1
PCDD, ng kWh^{-1}	0.5	2.5	0.6	0.4	0.3	0.1	0.1	0.2	1.5	0.5	1.5	0.1
PCDD/F WHO-TEQ, ng kWh^{-1}	0.1	0.4	0.1	0.1	0.1	0.03	0.03	0.04	0.13	0.04	0.08	0.01
HCB, ng kWh^{-1}	35	500	51	34	<16	<4	<4	<6	210	<0.4	<1	23
Total PCB, ng kWh^{-1}	190	950	200	160	125	30	31	92	- [b]	177	387	123
PCB WHO-TEQ, ng kWh^{-1}	0.002	0.01	0.002	0.002	0.004	0.001	0.001	0.002	0.003	0.002	0.006	0.003

[a] Note ss = steady-state engine load, stm = start-up and manoeuvring i.e. low and variable engine load.

[b] Analysis not possible.

3.3. Comparison with previous studies

The levels of the PCDD/PCDF emissions determined in this study are in good agreement (but slightly lower) with those reported by Lloyds in the 1990's (Lloyd's Register Engineering Services, 1993; Compaan et al., 1992). For 3 different ships, 6 exhaust samples were analysed in the Lloyds investigation. Rather than emissions, their results were expressed as concentrations in PCDD/PCDF International-TEQ in ng m^{-3}: 0.002 – 0.22 (range for four samples from diesel engines using residual oils) and 0.01 - 0.04 (for gasoil powered engines). Note that in contrast to the present work, the analysed data in the Lloyds investigation were corrected for recoveries of the internal standards. These can be compared with the equivalent PCDD/PCDF WHO-TEQ concentrations TEQ (ng m^{-3}) determined in this study: 0.005 – 0.03 (ships A, B and C, with residual oils) and 0.003 – 0.005 (ships A and C, for gasoil).

Recently national PCDD/PCDF emissions from diesel road vehicles were assessed (Kindbom et al., 2004) and found to lie around 0.024 – 0.1 µg TEQ ton^{-1}. By assuming a heating value of 12 kWh kg^{-1} for road diesel fuel and a 45% efficiency for the diesel engine, these values correspond to 0.004 – 0.02 ng TEQ kWh^{-1}. This range is slightly lower than the emissions factor, 0.03 ng TEQ kWh^{-1}, proposed in the present study for marine distillates, i.e. marine diesel and marine gasoil (Table 6).

The measured exhaust HCB and PCB ng kWh^{-1} emissions (<6 – 23 and 92 – 123 for gasoil, and, <0.4 - 500 and 30 – 950 for residual oil) in this work compare reasonably well to previous measurements on two ferries in 1994 (Cooper, 1996): 2.2 (HCB) and 120 (PCB) for a gasoil driven diesel engine, and 9.0 (HCB) and 120 (PCB) for a residual oil diesel engine (in ng kWh^{-1}). Some HCB and PCB samples were even analysed in the same Lloyds micro-contaminant investigation mentioned above. For HCB, their results were 3.7 ng m^{-3} (for one gasoil powered engine sample) and 0.4 – 2.3 ng m^{-3} (range for two samples from diesel engines using residual oils). For PCB (sum of 14 PCBs mostly indicator PCBs), the corresponding concentrations were 82 – 265 ng m^{-3} (two gasoil engine samples) and 26 – 58 ng m^{-3} (two residual oil engine samples). The equivalent HCB and PCB exhaust concentrations determined in this study were 1 – 5 and 11 - 27 ng m^{-3} for gasoil, and, <0.1 - 36 and 5 – 68 ng m^{-3} for residual oil respectively.

3.4. HCB, PCB, PCDD and PCDF Emission factors

Based on the results of this project and with regard to previous work, a revision of suitable emission factors for emission inventories can be suggested (Table 6). The data presented in Table 6 can be compared to previous marine emission factors assignments made for HCB as 8 ng/kWh, Total PCB as 100 ng/kWh and PCDD/PCDF I-TEQ as 1 ng/kWh (Cooper and Gustafsson, 2004). Thus besides differentiating between fuel types, the present results suggest that a lower emission factor for PCDD/PCDF WHO-TEQ and a higher emission factor for HCB are probably more suitable. From the available results, there is no firm rationale for differentiating the emission factors for engine types regarding engine speed.

In general, the measured emissions can be considered as relatively very low. To illustrate this, the PCDD/PCDF emission factor for residual oil in Table 6 corresponds to ca. 0.5 ng TEQ kg^{-1} fuel. This can be compared to emissions from known significant sources, for example forest fires, 20 ng TEQ kg^{-1} (Gullett and Touati, 2003), large-scale biomass combustion, 1.7 ng TEQ kg^{-1}, and municipal solid waste combustion 1.3 ng TEQ kg^{-1} (Kindbom et al., 2004).

Table 6. HCB, PCB, PCDD and PCDF emissions factors for different marine fuels

		Marine Distillate		Residual Oil	
	Unit	ng kWh^{-1}	g TJ supplied $^{-1}$ [a]	ng kWh^{-1}	g TJ supplied $^{-1}$ [a]
HCB		20	1.95×10^{-3}	30	3.50×10^{-3}
Total PCB		90	8.76×10^{-3}	120	1.40×10^{-2}
PCDD/PCDF WHO-TEQ		0.03	2.92×10^{-6}	0.1	1.17×10^{-5}

[a] The conversion from ng kWh^{-1} to g TJ^{-1} supplied takes in to account the different diesel engine types and their distribution (corresponds to ca. 45% efficiency for the diesel engine).

3.5. Total emissions from Swedish sold marine fuels

One approach to reporting air emissions from "Swedish shipping" is based on combining activity data (from Swedish marine fuel sales) with pollutant specific, emission factors (EMEP, 2003; IPCC, 1997). This methodology, which follows international reporting requirements, has the advantage of providing a relatively easy, well-defined total emission calculation and thereby facilitates harmonisation when comparing emissions internationally. The main drawback however is that many ships use fuel purchased abroad that cause significant emissions around the Swedish coastline, which will not be accounted for. A second problem is that since the emissions are generated from data on Swedish marine fuel sales only, fluctuations in fuel prices abroad will effect the reported emissions. Thus a "decrease" in the annual emissions may simply be a result of cheaper fuel prices abroad and not due to reduced sea traffic or introduction of emission abatement technology.

Nevertheless Sweden is obligated to follow this approach for international reporting duties of "International sea traffic" and "National navigation" and it is therefore of interest to compute these "total Swedish emissions" using the derived emission factors in section 3.4 above. As illustrated by Table 7, the majority of the emissions are associated with International sea traffic and the use of residual oils. A note of caution should be added when interpreting Table 7 however. Although almost all International sea traffic is associated with larger ships (> 100 gross tonnage) operating on marine distillates and residual oils, this is not so for National navigation. In this case some of the fuel used will be by smaller vessels < 100 gross tonnage and some vessels are operated using petrol as a fuel in this category. Bearing this in mind, combining solely the emission factors in Table 7 (which have been derived for diesel engines for ships > 100 gross tonnage) with activity data (marine distillates and residual oils for national navigation) will yield emissions for “National Navigation” with a greater uncertainty. One should note that fuel use (and emissions) from the fishing fleet is poorly defined and not covered in the above source categories (forms part of “Other sectors” in the reporting protocol by Statistics Sweden). According to 2001 data from the Swedish National Board of Fisheries (Bengtsson and Brantäng, 2001), the fishing fleet consists of only 1 851 vessels with an installed machinery of 228 MW (27% associated with cod fishing). Based on estimates from a Life Cycle Assessment for Swedish cod fishing for 1999 (Ziegler, 2001), the fuel (marine distillates) consumption can be roughly estimated as ca. 71 ktons (i.e. 85 000 m^3).

Table 7. HCB, PCB, PCDD and PCDF emissions in grams from Swedish sold marine fuels for year 2002

	Sold amount, m^3	Energy equivalent, TJ	HCB, g	Total PCB, g	PCDD/PCDF, WHO-TEQ g
International sea traffic					
Residual oils [a]	1 182 267	46 731	100 - 230	390 - 920	0.32 - 0.77
Marine distillates [b]	174 767	6 404	7 – 17	34 - 79	0.011 - 0.026
National Navigation					
Residual oils [a]	48 777	1 928	4 - 9	16 - 38	0.014 - 0.032
Marine distillates [b]	123 893	4 540	5 - 12	24 - 56	0.008 - 0.019
Fishing					
Marine distillates [c]	85 000	3032	4 - 8	16 - 37	0.005 - 0.012
TOTALS			120 - 280	480 - 1100	0.37 - 0.85

[a] Corresponds to sales of Eo2, Eo3, Eo4, Eo5 and Eo6 fuels as registered by Statistics Sweden.

[b] Corresponds to sales of diesel and Eo1 fuels as registered by Statistics Sweden.

[c] Rough estimate based on combining data from 1999 and 2001.

The values in Table 7 can be compared with previously reported national estimates of PCDD/PCDF emissions from “Swedish marine traffic” as 0.1 – 7 g PCDD/PCDF Nordic TEQ per year for the years 1993 – 1995, (Quass et al., 2000). In the same reference, Swedish national total emissions are reported as 94 – 212 g PCDD/PCDF International TEQ for 1987, 17 – 77 g PCDD/PCDF Nordic TEQ for 1993 and 26 – 98 PCDD/PCDF International TEQ for 2000. A more recent review has illustrated the decline in national emissions over the period 1980 – 2001, where from 1997 – 2001 the emissions have been reasonably stable at around 40 – 45 g PCDD/PCDF TEQ (Kindbom et al., 2004). For the year 2002 emission reporting, PCDD/PCDF are estimated as ca. 45 g TEQ, but both PCB and HCB were not estimated. Consequently, at least PCDD/PCDF emissions from Swedish marine fuel sales are relatively small i.e. only 1 – 2% of the national total. Some Swedish emission data for HCB and PCB for the year 1995 has however been complied previously and reported as 161 and 2 022 kg year^{-1} respectively (Meteorological Synthesizing Centre East, 1995). Thus ship emissions of HCB and PCB are also likely to be very small relative to the national totals.

Recently the US Environmental Protection Agency presented emission inventories of these species concerning disposal on and off site, and other releases in the USA (US EPA, 2002). Thus for year 2002 the total emissions of HCB, PCB and PCDD/PCDF (classed as "dioxin and dioxin-like substances") were reported as 7.6 x 10^6, 8.7 x 10^8, and 1.4 x 10^5 grams.

3.6. Total emissions within areas of national importance

In addition to the international reporting duties outlined in section 3.5 above, an alternative calculation in assigning Swedish marine emissions is periodically undertaken by the Swedish Maritime Administration (Swedish Maritime Administration, 2003). It is important to note that for this purpose both the boundaries and calculation methodology differ significantly from those for the international reporting obligations. The main difference is that the geographical emission boundaries are more "morally" representative of the Swedish emissions and the calculation methodology is based on a so-called "bottom-up approach" using a ship movement database. Specifically, fuel consumption data from fuel sales delivery data are not used in these calculations and instead the fuel consumption (irrespective of where the fuel was purchased) for an individual ship movement is calculated as an intricate function of engine type, ship type, route etc. A disadvantage with this "bottom-up approach" is that although well intended regarding improved accuracy and completeness, a substantial effort is necessary to fully complete such a model and thereafter maintain it. In practice, these emission estimates are considered as quite uncertain due largely to the quality of the input data but they do however constitute the best current estimate for these regions.

By using the reported CO_2 emissions (Swedish Maritime Administration, 2003), one can indirectly calculate the fuel consumed in the assigned regions and thereby the HCB, PCB, PCDD and PCDF emissions (Table 8). For this exercise it can be assumed that the carbon content of all fuels is 86.7% (Cooper and Gustafsson, 2004) and that the fuel equivalents consist of 82% residual oils and 18% marine distillates (based partly on Table 7). Relative to the national total, ca. 45 g PCDD/PCDF TEQ (Kindbom et al., 2004), these emissions can also be considered as small.

Table 8. HCB, PCB, PCDD and PCDF emissions in grams from Swedish and international shipping in areas of national importance for year 2002

	CO_2 emissions, kton	Fuel equiv., kton	HCB, g	Total PCB, g	PCDD/ PCDF, WHO-TEQ g
North Sea and Baltic Sea	35 000	11 010	880 - 2 040	3 600 - 8 300	2.7 - 6.4
Baltic Sea	17 000	5 348	730 - 990	1 700 – 4 000	1.3 - 3.1
Baltic Sea with calls at Sweden	5 200	1 636	130 - 300	530 – 1 230	0.4 - 1.0
"Swedish fraction" [a]	2 800	881	70 - 160	280 - 660	0.2 - 0.5

[a] Corresponds to half of the voyage distance for sea traffic in the Baltic Sea calling at Sweden.

3.7. Emissions from other diesel engines

Recently, national PCDD/PCDF emissions from diesel road vehicles were assessed (Kindbom et al., 2004) and found to lie around 0.024 – 0.1 µg ton^{-1} fuel. In calculating the PCDD/PCDF emissions from road vehicles with diesel engines an emission factor of 0.1 µg ton^{-1} fuel was used. For year 2002, diesel consumption by road vehicles in Sweden was 2 490 355 m^3 or ca. 2.02 x 10^6 tons (Gustafsson, T., 2004). Based on these figures, a total emission of 0.202 g TEQ year^{-1} (± 40 relative %) for diesel road vehicles can be calculated.

In addition to diesel driven road vehicles, there are several other types of vehicles using diesel engines classed as; off-road diesel machinery (tractors, forest harvesting trucks, container loaders etc.), military vehicles and railway locomotives. Regarding the emission factors for these sources, it is reasonable to assume the same factor as road vehicles (at least until new measurement data specifies otherwise) since they use a similar low aromatic, low sulphur diesel fuel, environmental class 1 diesel (Mk1). The 2002 diesel quantities consumed for off-road, military vehicles and locomotives were reported as 10 316, 1 141 580 and 26 700 m^3 (Gustafsson, T., 2004) which corresponds to total PCDD/PCDF emissions of 0.00083, 0.092 and 0.0022 g TEQ year^{-1} (± 40 relative %) respectively.

Thus for Swedish sold fuels, ships account for ca. 0.37 – 0.85 g TEQ year^{-1} of PCDD/PCDF emissions (Table 7) while other land-based diesel engines contribute an additional 0.18 – 0.42 g TEQ year^{-1}.

4. Conclusions

The measurement data obtained in this study has enabled an improved assignment of emission factors for HCB, PCB, and PCDD/PCDF as a function of fuel type. In turn, this provides a refined reference material to provide more reliable estimates of these species in future emission inventory and modelling studies. The central conclusion however, drawn from the results of this work is that that the contribution of PCCD/PCDDF exhaust emissions from ships is relatively small (i.e. 1 – 2% of the national total for 2002). Similarly HCB and PCB emissions for 2002 are also probably very small compared to national totals estimated in 1995. This is also in line with the findings of the first appraisal of these emissions in the early 1990s.

Emissions from other diesel engines in Sweden (road and military vehicles, off-road machinery and locomotives) are also estimated as being very small. PCDD/PCDF emissions from all diesel engines (marine and land transport sectors) using Swedish sold fuel can be calculated as ca. 0.9 g TEQ year^{-1}. The uncertainty with this value is however probably significant (ca. ± 40% at 95% confidence interval) in light of the relatively limited database and inherent measurement uncertainties.

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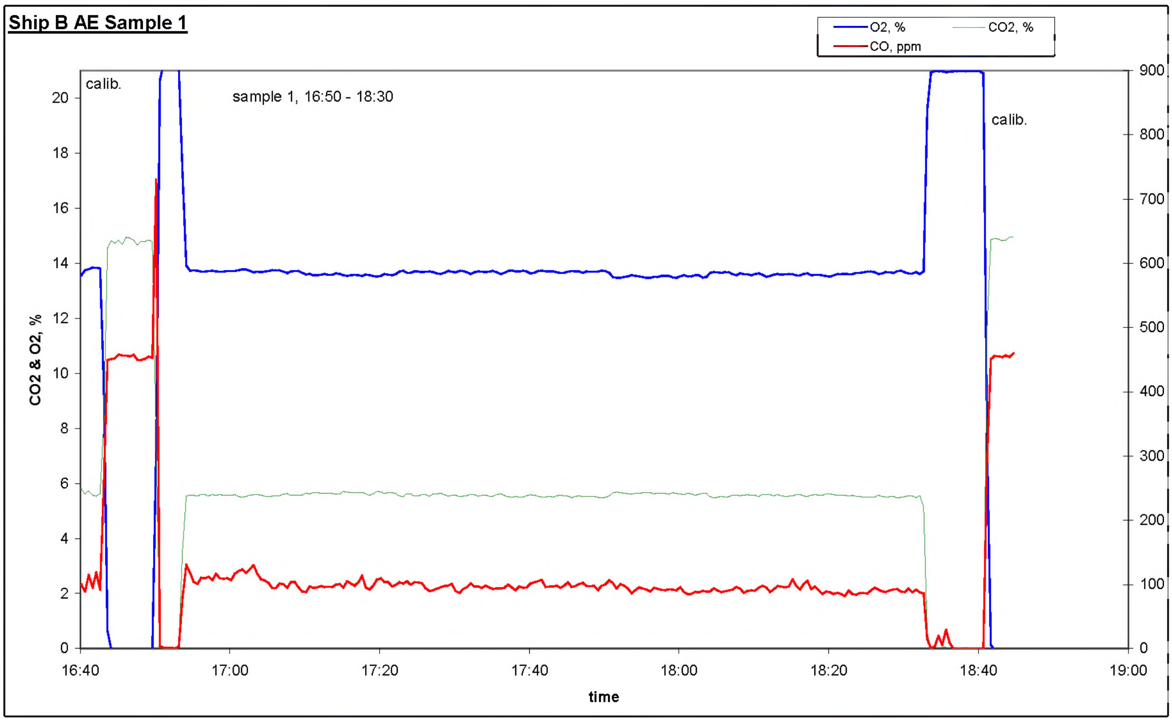
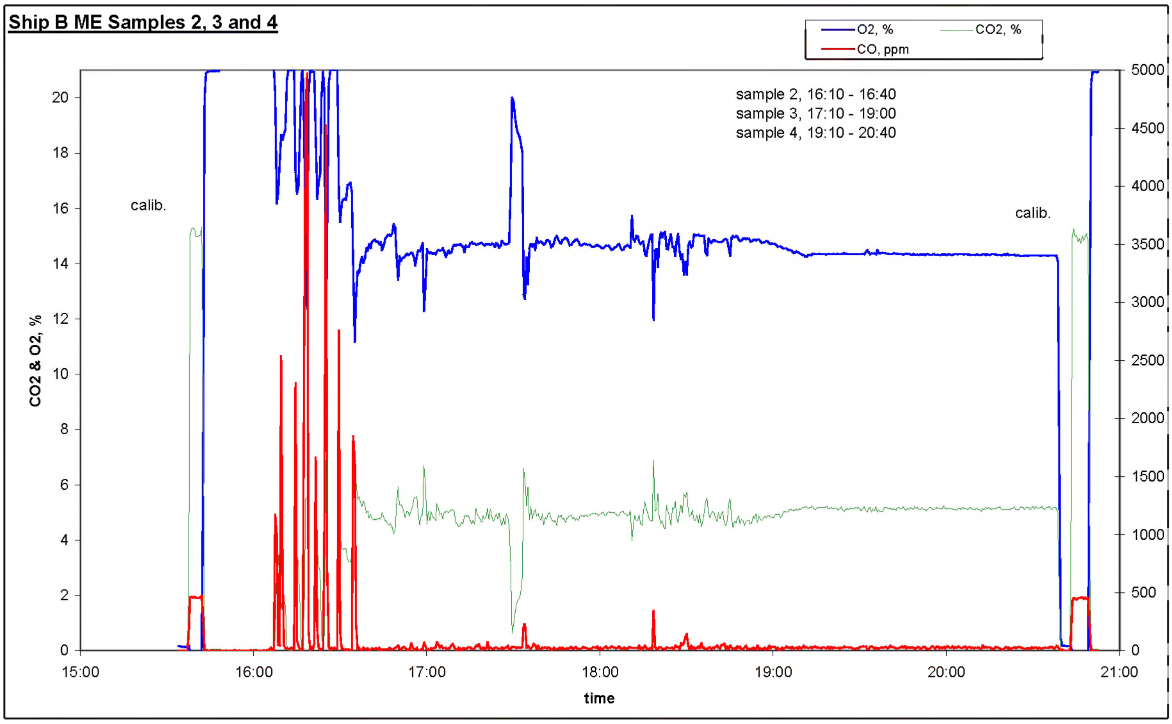
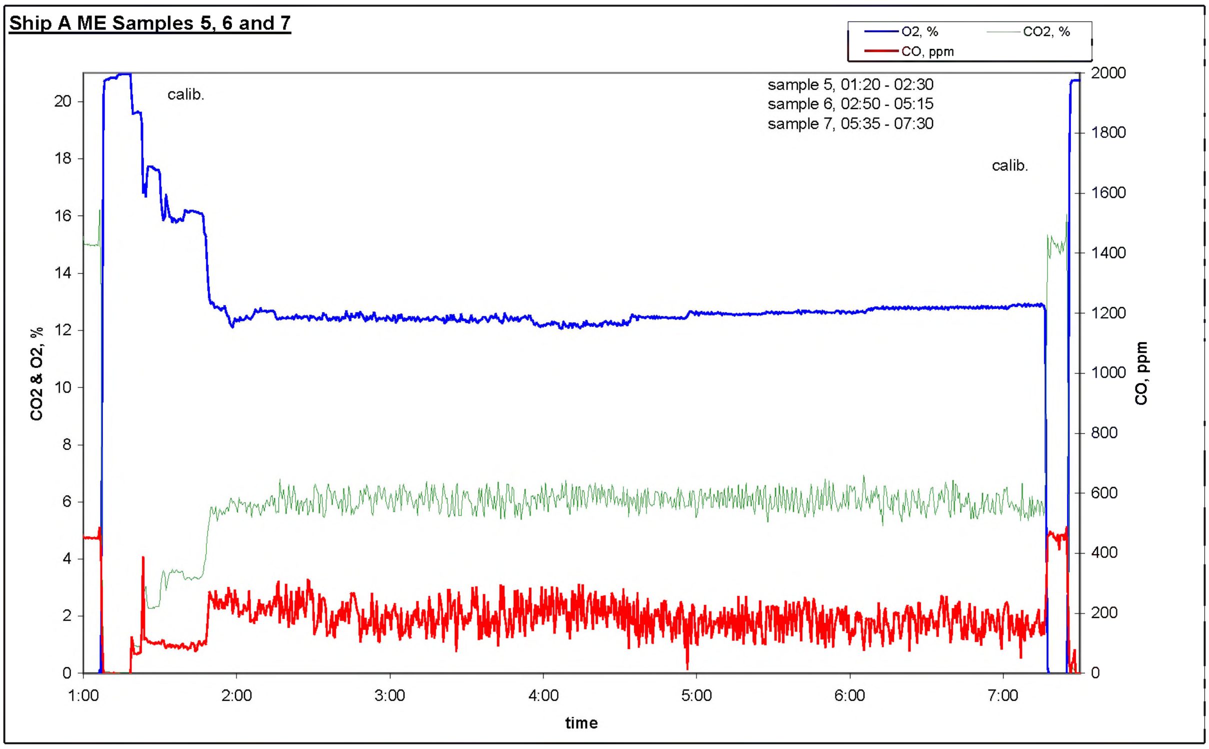
Appendix 1 CO, CO_2 and O_2 concentration profiles of the sampling periods






Ship A ME Samples 5, 6 and 7
O2, %
CO2, %
CO, ppm
calib.
sample 5, 01:20 - 02:30
sample 6, 02:50 - 05:15
sample 7, 05:35 - 07:30
calib.
CO2 & O2, %
0
2
4
6
8
10
12
14
16
18
20
CO, ppm
0
200
400
600
800
1000
1200
1400
1600
1800
2000
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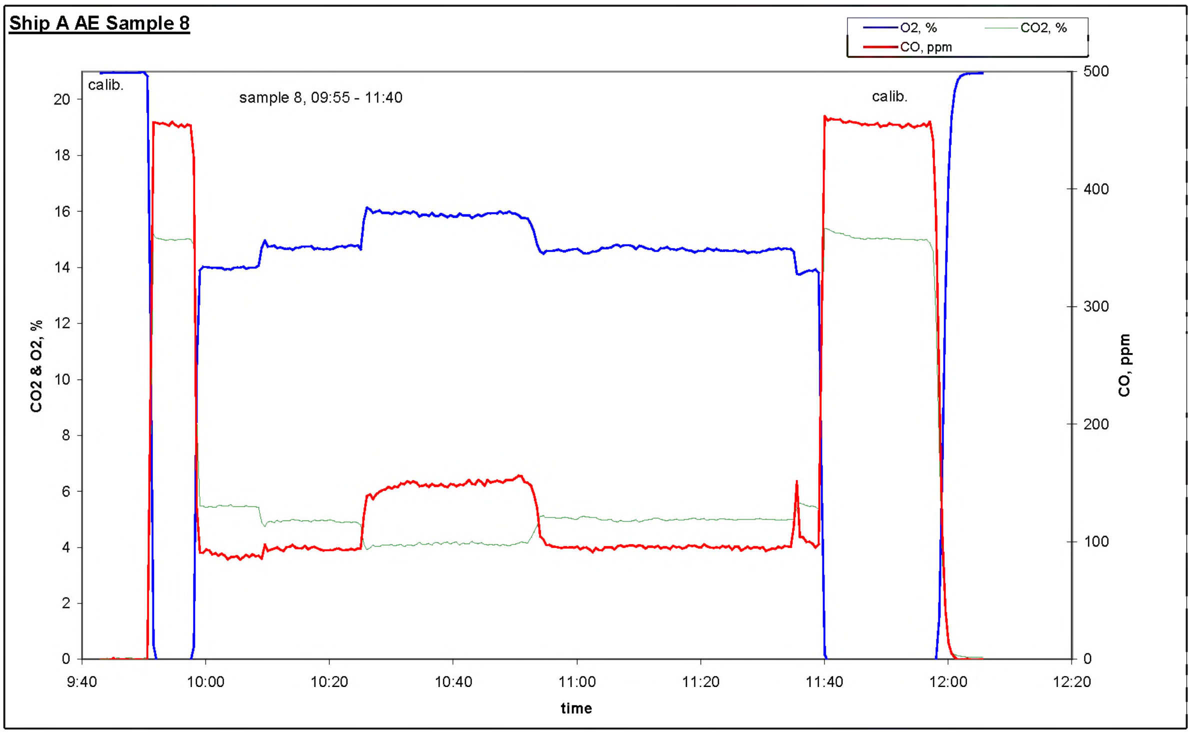
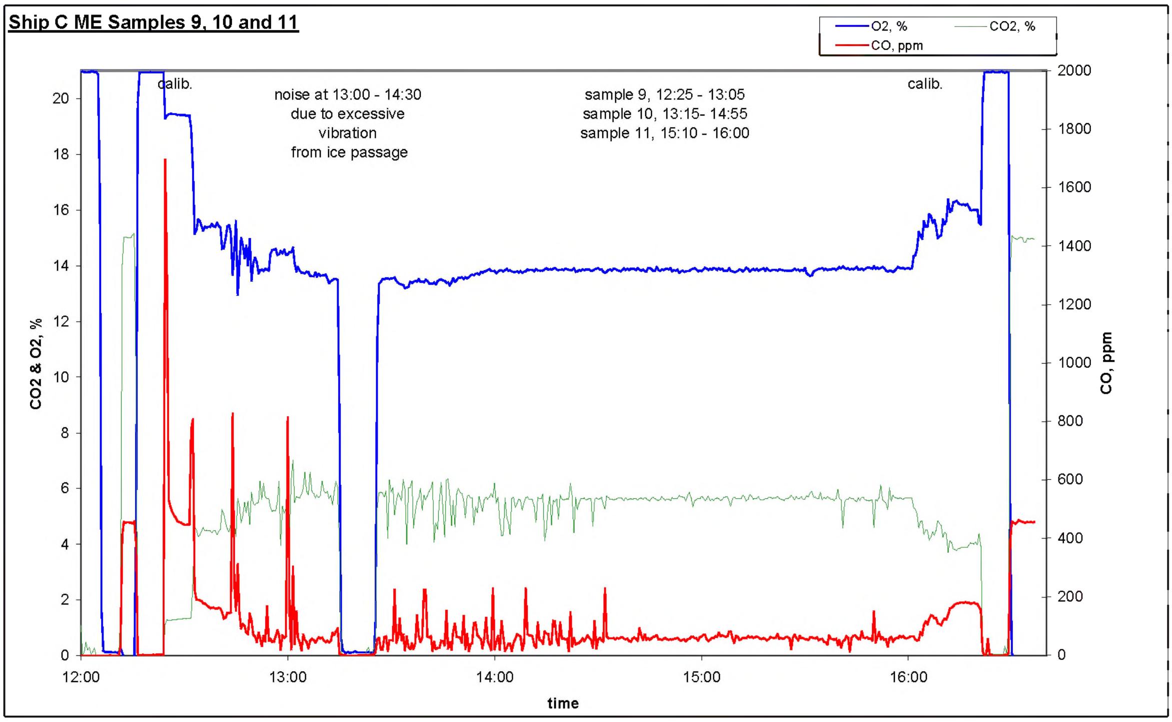
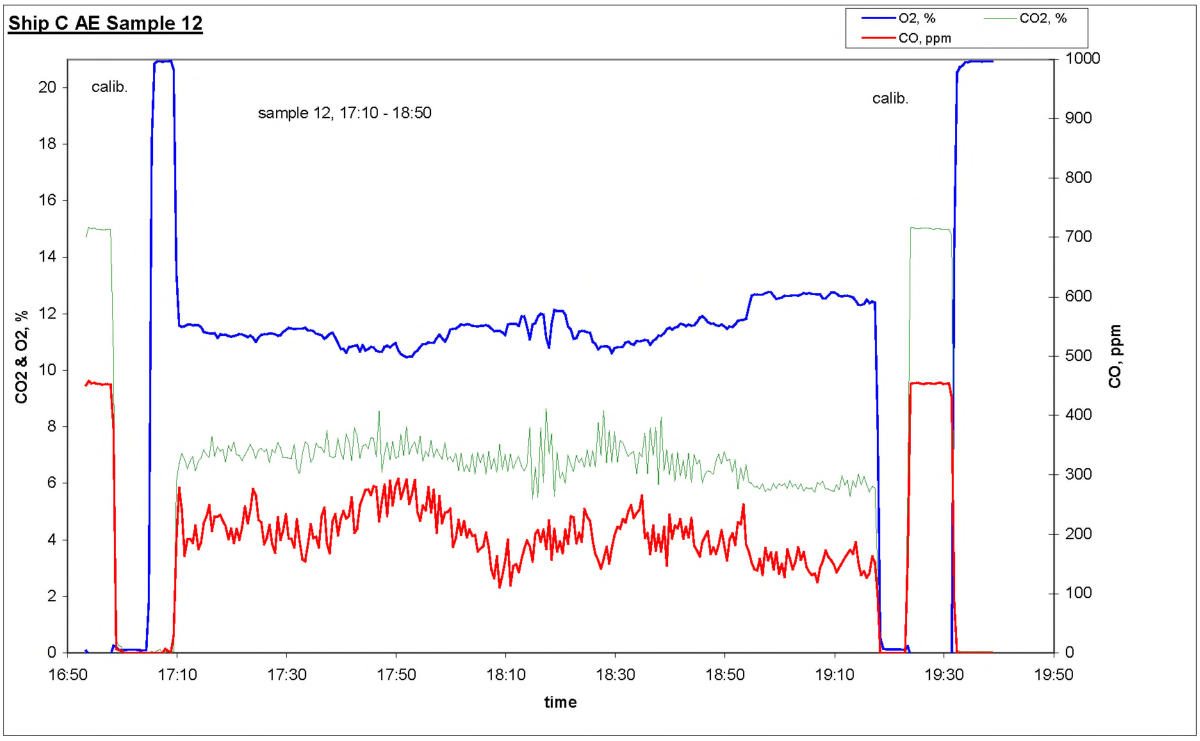
2:00
3:00
4:00
5:00
6:00
7:00
time


Ship A AE Sample 8
O2, %
CO2, %
CO, ppm
calib.
sample 8, 09:55 - 11:40
calib.
CO2 & O2, %
0
2
4
6
8
10
12
14
16
18
20
CO, ppm
0
100
200
300
400
500
9:40
10:00
10:20
10:40
11:00
11:20
11:40
12:00
12:20
time


Ship C ME Samples 9, 10 and 11
O2, %
CO2, %
CO, ppm
calib.
noise at 13:00 - 14:30
due to excessive
vibration
from ice passage
sample 9, 12:25 - 13:05
sample 10, 13:15- 14:55
sample 11, 15:10 - 16:00
calib.
CO2 & O2, %
0
2
4
6
8
10
12
14
16
18
20
CO, ppm
0
200
400
600
800
1000
1200
1400
1600
1800
2000
12:00
13:00
14:00
15:00
16:00
time


Ship C AE Sample 12
O2, %
CO2, %
CO, ppm
calib.
sample 12, 17:10 - 18:50
calib.
CO2 & O2, %
0
2
4
6
8
10
12
14
16
18
20
CO, ppm
0
100
200
300
400
500
600
700
800
900
1000
16:50
17:10
17:30
17:50
18:10
18:30
18:50
19:10
19:30
19:50
time

Appendix 2 Speciated PCB, PCDD and PCDF emissions

Table A2.1
Speciated PCDD (dioxins) and PCDF (furans) for the fuel oil and lubrication oil samples (µg kg^{-1})

	Ship A (ME)	Ship B (ME and AE)	Ship C (AE)	Ship B (ME)	Ship C (ME)	Ship C (AE)
Type of fuel / lub. oil	RO	RO	MGO	Dirty lub.	Dirty lub.	Clean lub.
Sample identification	FO3	FO1	FO4	SO1	SO4	SO3
2,3,7,8-tetraCCD	<0.004	<0.001	<0.004	<0.002	<0.004	<0.005
1,2,3,7,8-pentaCCD	<0.005	0.078	<0.005	0.014	<0.005	<0.01
1,2,3,4,7,8-hexaCCD	<0.007	0.077	<0.007	0.005	<0.007	0.021
1,2,3,6,7,8-hexaCCD	<0.007	0.11	<0.007	0.005	<0.007	0.033
1,2,3,7,8,9-hexaCCD	<0.007	0.055	<0.007	0.004	<0.007	0.021
1,2,3,4,6,7,8-heptaCCD	0.011	0.12	0.022	0.006	0.013	0.045
Octachlordibenzodioxin	0.067	0.11	0.054	0.006	0.078	0.065
2,3,7,8-tetraCDF	<0.003	<0.02	<0.003	<0.01	0.006	<0.003
1,2,3,7,8-pentaCDF	<0.003	0.098	<0.003	0.015	<0.003	0.020
2,3,4,7,8-pentaCDF	<0.003	0.074	0.007	0.012	<0.003	0.017
1,2,3,4,7,8-hexaCDF	<0.005	0.008	<0.005	0.004	<0.005	0.022
1,2,3,6,7,8-hexaCDF	<0.005	0.003	<0.005	0.002	<0.005	0.025
1,2,3,7,8,9-hexaCDF	0.006	0.059	<0.005	0.004	<0.005	0.012
2,3,4,6,7,8-hexaCDF	<0.005	0.068	<0.005	0.006	0.019	0.031
1,2,3,4,6,7,8-heptaCDF	<0.008	0.11	<0.008	0.006	<0.008	0.093
1,2,3,4,7,8,9-heptaCDF	<0.008	0.080	<0.008	0.003	<0.008	0.026
Octachlordibenzofuran	<0.003	0.096	0.062	<0.01	<0.03	0.033

Table A2.2

Speciated PCB for the fuel oil and lubrication oil samples (µg kg^{-1})

	Ship A (ME)	Ship B (ME and AE)	Ship C (AE)	Ship B (ME)	Ship C (ME)	Ship C (AE)
Type of fuel / lub. oil	RO	RO	MGO	Dirty lub.	Dirty lub.	Clean lub.
Sample identification	FO3	FO1	FO4	SO1	SO4	SO3
Planar PCB 77	0.010	<0.04	0.018	<0.01	0.004	0.004
Planar PCB 126	<0.005	<0.02	0.062	<0.01	0.003	0.010
Planar PCB 169	<0.005	<0.03	0.015	<0.01	0.006	0.010
Planar PCB 81	0.002	<0.06	0.004	<0.01	0.007	0.001
Planar PCB 105	0.038	0.30	<0.007	0.028	0.012	0.020
Planar PCB 114	0.026	0.042	<0.003	<0.01	0.006	0.039
Planar PCB 118	0.071	0.48	0.31	0.087	0.047	0.14
Planar PCB 123	<0.006	0.20	<0.003	<0.01	0.003	0.047
Planar PCB 156	0.029	<0.06	<0.003	<0.02	0.012	0.021
Planar PCB 157	0.008	<0.06	<0.003	<0.01	<0.003	<0.003
Planar PCB 167	0.050	0.065	<0.004	<0.02	0.009	0.020
Planar PCB 189	<0.005	<0.03	<0.003	<0.02	<0.003	<0.003
Indicator PCB 28	9.4	0.60	- [a]	1.06	5.2	6.4
Indicator PCB 52	0.37	0.79	1.3	0.97	0.43	0.43
Indicator PCB 101	0.33	1.3	0.29	0.55	0.29	0.3
Indicator PCB 118	0.071	0.48	0.31	0.087	0.047	0.14
Indicator PCB 138	0.41	0.40	0.53	0.10	<0.01	<0.01
Indicator PCB 153	0.27	0.49	0.25	0.16	0.25	0.16
Indicator PCB 180	<0.01	0.089	0.13	<0.02	<0.01	<0.01

[a] Analysis not possible.

Table A2.3

Speciated PCDD (dioxins) and PCDF (furans) for the exhaust samples (ng kWh^{-1})

Ship / engine	B / AE	B / ME	B / ME	B / ME	A / ME	A / ME	A / ME	A / AE	C / ME	C / ME	C / ME	C / AE
Operation [a]	ss	stm	ss	ss	stm	Ss	ss	ss	stm	ss	ss	ss
Fuel type	RO	RO	RO	RO	RO	RO	RO	MGO	RO	RO	RO	MGO
Sample id.	1	2	3	4	5	6	7	8	9	10	11	12
2,3,7,8-tetraCCD	<0.012	<0.060	<0.008	<0.007	<0.039	<0.010	<0.010	<0.015	<0.016	<0.004	<0.006	<0.003
1,2,3,7,8-pentaCCD	0.032	0.13	0.033	0.018	<0.079	<0.020	<0.020	<0.030	0.041	0.018	0.031	<0.005
1,2,3,4,7,8-hexaCCD	0.025	0.14	0.023	0.018	<0.063	<0.016	<0.016	<0.024	0.041	<0.006	0.019	0.007
1,2,3,6,7,8-hexaCCD	0.025	0.12	0.035	0.021	<0.063	<0.016	<0.016	<0.024	0.049	<0.006	0.025	<0.005
1,2,3,7,8,9-hexaCCD	0.022	0.12	0.026	0.020	<0.063	<0.016	<0.016	<0.024	<0.025	<0.006	0.015	<0.005
1,2,3,4,6,7,8-heptaCCD	0.062	0.27	0.068	0.037	<0.079	<0.020	<0.020	<0.030	0.132	0.026	0.077	<0.007
Octachlordibenzodioxin	0.085	0.44	0.11	0.070	0.34	0.094	0.061	0.17	0.346	0.079	0.22	<0.012
2,3,7,8-tetraCDF	0.039	0.11	0.028	0.024	<0.055	<0.014	<0.014	<0.021	0.066	0.016	0.040	0.012
1,2,3,7,8-pentaCDF	0.043	0.19	0.059	0.025	<0.079	<0.020	<0.020	<0.030	0.066	0.016	0.053	<0.008
2,3,4,7,8-pentaCDF	0.051	0.16	0.053	0.024	<0.079	<0.020	<0.020	<0.030	0.066	0.014	0.028	<0.008
1,2,3,4,7,8-hexaCDF	0.036	0.17	0.060	0.024	<0.039	<0.010	<0.010	<0.015	0.049	0.014	0.046	<0.003
1,2,3,6,7,8-hexaCDF	0.029	0.31	0.079	0.050	<0.039	<0.010	<0.010	<0.015	0.033	0.010	0.028	<0.003
1,2,3,7,8,9-hexaCDF	0.027	0.16	0.035	0.023	<0.039	<0.010	<0.010	<0.015	0.066	0.018	0.043	0.008
2,3,4,6,7,8-hexaCDF	0.045	0.22	0.048	0.028	<0.039	<0.010	<0.010	<0.015	0.091	0.010	0.009	0.008
1,2,3,4,6,7,8-heptaCDF	0.074	0.36	0.096	0.049	<0.079	0.063	0.029	0.043	0.132	0.049	0.17	0.012
1,2,3,4,7,8,9-heptaCDF	0.021	0.11	0.032	0.015	<0.079	0.016	<0.020	<0.030	0.033	0.014	0.022	<0.005
Octachlordibenzofuran	0.058	0.36	0.051	0.048	<0.16	0.027	<0.040	0.062	<0.082	0.059	<0.031	<0.017

[a] Note ss = steady-state engine load, stm = start-up and manoeuvring i.e. low and variable engine load.

Table A2.4

Speciated PCB emissions for the exhaust samples (ng kWh^{-1})

Ship / engine	B / AE	B / ME	B / ME	B / ME	A / ME	A / ME	A / ME	A / AE	C / ME	C / ME	C / ME	C / AE
Operation	ss	stm	ss	ss	stm	ss	ss	ss	stm	ss	ss	Ss
Fuel type	RO	RO	RO	RO	RO	RO	RO	MGO	RO	RO	RO	MGO
Sample id.	1	2	3	4	5	6	7	8	9	10	11	12
Planar PCB 77	0.15	0.86	0.14	0.12	0.15	0.041	0.038	0.098	0.64	0.098	0.20	0.14
Planar PCB 126	0.016	0.076	0.010	0.012	0.024	0.008	0.006	0.009	0.041	0.014	0.062	0.033
Planar PCB 169	0.005	0.030	0.010	0.007	0.016	0.004	0.004	0.003	0.016	0.008	0.043	0.023
Planar PCB 81	0.021	0.12	0.023	0.017	0.032	0.008	0.008	0.015	0.041	0.004	0.015	0.007
Planar PCB 105	0.69	3.6	0.64	0.58	1.1	0.074	0.26	0.77	1.3	0.22	0.43	0.35
Planar PCB 114	0.13	0.48	0.12	0.11	0.15	0.018	0.020	0.14	0.21	0.081	0.059	0.035
Planar PCB 118	2.6	12	2.4	1.8	2.1	0.42	0.50	1.4	0.25	0.51	0.74	0.60
Planar PCB 123	0.47	2.1	0.46	0.39	0.32	0.068	0.091	0.27	0.39	0.020	0.068	0.017
Planar PCB 156	0.30	1.1	0.24	0.19	0.47	0.14	0.15	0.44	0.56	0.11	0.20	0.13
Planar PCB 157	0.072	0.24	0.094	0.062	0.21	0.039	0.040	0.089	0.082	0.018	0.040	0.022
Planar PCB 167	0.13	0.50	0.15	0.12	0.19	0.038	0.049	0.089	0.53	0.12	0.11	0.063
Planar PCB 189	0.035	0.14	0.033	0.026	0.079	0.018	0.020	0.030	0.11	0.018	0.034	0.013
Indicator PCB 28	37	210	42	38	23	6.3	5.3	15	- [a]	20	30	33
Indicator PCB 52	9.0	44	8.7	6.2	6.3	1.7	1.7	5.0	- [a]	1.6	1.6	2.7
Indicator PCB 101	9.0	34	7.0	4.4	5.1	1.2	1.4	4.1	- [a]	1.1	1.0	1.8
Indicator PCB 118	2.6	12	2.4	1.8	2.1	0.42	0.50	1.4	0.25	0.25	0.24	0.36
Indicator PCB 138	5.6	22	4.9	3.6	3.4	0.89	1.0	2.2	- [a]	0.62	0.91	1.2
Indicator PCB 153	5.5	23	5.0	3.3	4.2	0.98	1.1	2.9	- [a]	0.67	0.78	1.2
Indicator PCB 180	1.4	5.9	1.3	1.1	1.7	0.42	0.46	1.0	- [a]	0.32	0.34	0.32

[a] Analysis not possible.

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IVL Svenska Miljöinstitutet AB

IVL Swedish Environmental Research Institute Ltd

P.O. Box 210 60, SE-100 31 Stockholm
Hälsingegatan 43, Stockholm
Tel:: +46 (0)8 598 563 00
Fax: +46 (0) 8 598 563 90

P.O. Box 5302, SE-400 14 Göteborg
Aschebergsgatan 44
Tel:: +46 (0)31 725 62 00
Fax: +46 (0)31 725 62 90

www.ivl.se