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MONITORING OF SOME MAJOR VOLATILE ORGANIC COMPOUNDS ON BOARD OF CHEMICAL TANKERS

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ABSTRACT

Nowadays, chemical tankers are transporting a wide variety of chemical products. These products have different characteristics, and some are toxic. In literature several studies suggest an increased incidence of various forms of cancer for crew members on tankers. Most of these studies are based on medical statistics, rather than on effective measurements on board. The aim of this study is to monitor the average concentrations of toxic vapours on board of chemical tankers. Therefore we went on board of two chemical tankers for a 14-day trip and performed measurements during the normal operation of the vessel, in order to find out whether cargo vapours are traceable in the atmosphere in and around the vessel. The concentrations measured clearly show that there is a relationship between the cargoes transported and the concentration of the cargo vapour in the atmosphere in and around the vessel. The results further show an elevated concentration of the analyzed substances in the engine room and an important influence of the relative wind direction. Tank vents situated in the gas-safe zone influenced the results as well.

Keywords: shipboard conditions, diffusive monitoring, occupational health, BTEX.

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INTRODUCTION

Numerous gas and chemical tankers transport a wide variety of chemicals to feed the economy. It is inevitable that during common operations toxic cargo vapours are released into the atmosphere. But no recent data on their concentration in the atmosphere in and around ships are available.

In the literature there are several studies suggesting a causal relation between sailing as a crew member on tankers and the incidence of various forms of cancer (e.g. *Nilsson et al., 1998; Saarni et al., 2002).* Most of these studies are based on medical statistics. Only a few researchers went effectively on board to perform sampling and to identify the possible cause. The study of *Moen et al. (1995a)* was based on measurements of benzene performed on board. One can only hope that the high concentrations measured at that time have generally decreased thanks to improved operation procedures. Examples are closed gauging, loading with high velocity valves or, even better, with the use of a vapour return. In the case of high velocity valves, however, the released vapours are still present in the atmosphere nearby the ship. Our interest is whether we could find any traces of these vapours back on board. Especially the study published in the *International Safety Guide for Oil Terminals and Tankers, ISGOTT (ICS, OCIMF and IAPH (2006))* concerning air dispersion, may create some doubts. This study shows the air circulation around the ship's superstructure. It might be possible that parts of the cargo vapours released ahead of the superstructure are transported behind it by natural air circulation. The inlets of the ventilation for the accommodation (AC) and the engine room (ER) are situated at the aft end of the superstructure. One can assume that parts of these toxic vapours are being sucked by the ventilation intake. Also the flue gasses from the ship's engines as well as the vents of the different bunker tanks can be considered as a possible source of toxic vapours. To test this assumption was the main drive for our investigation.

Another item that can be questioned is whether the segregation between the gas-dangerous (gdz) and the gas-safe zone (gsz) is as well defined as mentioned in the international bulk chemical code (IBC)(*IMO, (2007)*). This subdivision is illustrated in Figure 1.

The aim of this study is to give a general overview of the concentrations of the toxic vapours at different locations on board, in various situations. In a later cam-

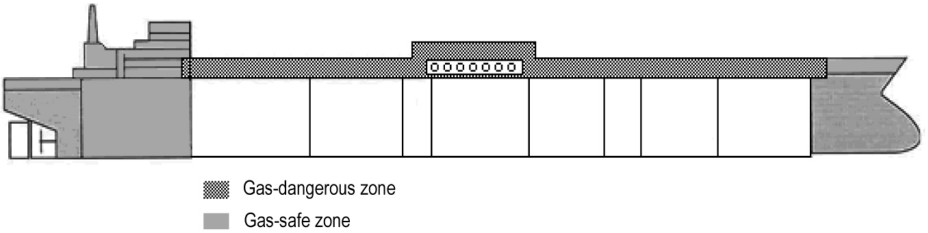

Figure 1: Gas-dangerous and gas-safe zones according to the IBC code

paign, we intend to study more in detail the concentrations in some specific spaces or zones that have been found interesting, based on the results of this campaign.

METHODS

Sampling and analytical methods

Diffusive sampling is particularly suited to determine time-weighted average volatile organic compound (VOC) concentration in occupational hygiene and environmental air monitoring *(Oury et al., 2006; Pennequin-Cardinal et al., 2005)*. Moreover it has as main advantages its simplicity and its cost effectiveness. Traditional diffusive sampling is characterized by low sampling rates and requires long sampling times. However, Radiello diffusive samplers are characterized by high and constant sampling rate values, high sensitivity and relatively short exposure times (Radiello Users Manual). The sampling rate is invariant towards humidity in the range 15-90% and wind speeds between 0.1 and 10 $m.s^{-1}$ (Radiello Users Manual). This method is also suitable for multipoint and simultaneous measurements. The used Radiello diffusive samplers consist of an adsorbing cartridge (530 mg of activated charcoal) inserted in a microporous polyethylene membrane. The diffusive sampler is exposed to air for a measured time period. The rate of sampling for a specific compound is determined by prior exposure in a standard atmosphere. VOCs migrate into the sampler by diffusion and are collected on the activated charcoal. In the laboratory, the collected material is desorbed by carbon disulfide. The solution is analyzed by gas chromatography coupled to mass spectrometry (GC-MS), according to a previously developed method *(Joos et al. 2003; Stranger, 2005)*.

A validation of this technique has been organized previously by our research group. Here all samples were collected in triplicate, with an extra annular denuder system nearby. The coefficients of variance, all having values below 10%, indicate the sufficient reproducibility for the collection of benzene, toluene, ethylbenzene and xylenes (BTEX) by means of Radiello passive samplers. The highest coefficients of variance, 12.2%, were calculated for the m+p-xylene determinations. However, all average BTEX concentrations agreed very well with the fixed monitor's results, as the ratios Radiello/denuder system were all close to one *(Stranger, 2005)*.

Also three blank cartridges were carried along with each vessel. They were kept sealed and stored near the cartridges that have been used. Later analysis showed that the readings of these blank samplers were all below the detection limits and so no correction had to be made on the obtained results.

To monitor all of the VOC compounds in air quantitatively is very time consuming and expensive. We have chosen 8 aromatic hydrocarbons based upon their presence in gasoline. As most cargoes are related to gasoline or are distillates from gasoline, and since gasoline is also used in the engine, we expected to find higher concentrations of these compounds on board. The compounds we analyzed the cartridges for were benzene, toluene, ethylbenzene, m+p-xylene, o-xylene, 1,3,5-trimethylbenzene (1,3,5-TMB) and 1,2,4- trimethylbenzene (1,2,4 -TMB). Acute (short-term) exposure to gasoline and its components benzene, toluene and xylenes has been associated with skin and sensory irritation, central nervous system (CNS) problems (tiredness, dizziness, headache, loss of coordination), effects on the respiratory system and eye and nose irritation. On top of skin, sensory and CNS problems, prolonged exposure to these compounds can also affect the kidney, liver and blood systems *(Agency for Toxic Substances and Disease Registry, 2004, 2007; Calabrese and Kenyon, 1991)*. These effects are also a justification for the choice of the 8 analyzed compounds.

The ships

We had access to two chemical tankers, sister ships, with a length of 112 m, equipped with 17 cargo tanks and an overall capacity of just less than 10,000 m^3. Both ships were trading between Rotterdam and the Baltic Sea area. The sampling places, chosen after a visit to the ships, are shown in Figure 2. These are the shelter on the maindeck, the manifold, the facing, the ventilation intake of the engine room (ER), the ventilation intake of the accommodation (AC), two different levels in the ER and two in the AC. In order to get an image as complete as possible of the concentrations, we took 63 samples per ship.

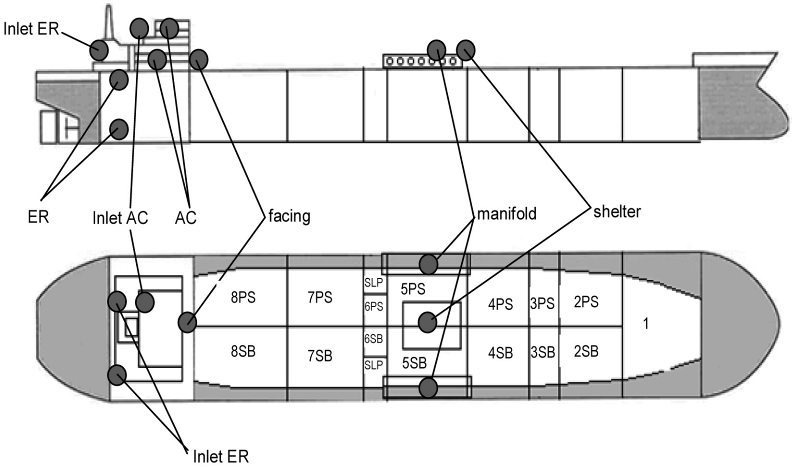

Figure 2: The location of the diffusive samplers on board.

PS = portside, looking from aft to forward the left side of the vessel.
SB = starboardside, looking from aft to forward the right side of the vessel

We made a logbook and a diary to keep records of the location of the tubes, the prevailing wind, weather conditions, voyage data, cargo operations, products on board, exposure time, etc. The temperature was automatically logged every 15 minutes.

Study protocol

We changed the Radiello® adsorbing cartridges every time the pilot came on board on arrival in port, and every time the pilot disembarked on departure from a port. This way of working resulted in separate measurements for the time in port and the time at sea. We expected the results for the time spent at sea to be different from the results for the time spent in port. Possible reasons for this difference might be the use of the main engine, influence from pollution sources ashore, influences from other vessels and the influence of cargo related operations. For vessel A we have data from 2 sea voyages and 3 ports, for vessel B data are available from 3 sea voyages and 3 ports.

For further classification of the results we divided a ship into four different areas. The first subdivision was in an indoor and outdoor area. Secondly indoor was split into AC and ER, outdoor in a gdz and a gsz. Indoor space was split into AC and ER, as the first one has to be considered as a living environment, the second one as a workplace. Outdoor was subdivided as specified in the IBC code, the international code for the construction and equipment of ships carrying dangerous chemicals in bulk (*IMO, 2007*). The gdz, being the area from forward to 3-5 m aft of the end of the superstructure facing the cargo area, and the gsz being the area from aft to 3-5 m aft of the end of

Table 1: Cargo handling during the measurement period.

Ship	Cargo	Tanks	Loading port to
Ship A	toluene	8PS	Antwerp to Rauma
	xylene	7PS	Rotterdam to Rauma
	ethanol	2PS, 4SB, 5PS, 5SB	Rotterdam to Rauma
	isopropyl alcohol IPA	6PS	Antwerp to Rauma
	butyl acrylate	3PS, 7SB	Rotterdam to Hamina
	monopropylene glycol	2SB	Rotterdam to Rauma
	varsol 40 (a)	3SB	Antwerp to Rauma
	exxsol D60 (b)	4PS	Antwerp to Rauma
	solvesso 150 (c)	6SB	Antwerp to Rauma
	solvesso 100 (c)	8SB	Antwerp to Rauma
Ship B	phenol	4PS, 4SB	Kotka to Rotterdam
	isoprene	1, 2PS	Kotka to Rotterdam
	paraffin C14-C17 (d)	3SB, 6SB, 7PS, 8PS, 8SB	Kotka to Rotterdam
	NPE-9 (e)	7SB	Kotka to Rotterdam
	NPE-10 (f)	5PS, 5SB	Kotka to Rotterdam
	NaOH	2PS, 2SB, 4PS, 4SB, 5PS	Wilhelmshaven to Kotka

(a): hydrocarbon aliphatic fluid, 16-20 wt % aromatic content, 41 $mg.kg^{-1}$ benzene content
(b): a complex mixture of aliphatic, cycloparaffinic hydrocarbons
(c): a highly refined lubricating mineral base oil, hydrocarbon fluid, with 34% weight 1,2,4-TMB
(d): heavy alkanes C14-C17
(e): nonylphenol + 9 EO polyethoxylate C9H19C6H4-O-(OCH2CH2)n-H (n=9)
(f): nonylphenol + 10 EO polyethoxylate C9H19C6H4-O-(OCH2CH2)n-H (n=10)

the superstructure facing the cargo area, are shown in Figure 1. In order to reduce the number of results, we often used average values for one zone or space.

Table 1 gives an overview of the different products carried by the two vessels during our campaign, with their respective stowage on board and loading and discharging port.

RESULTS

Port

In order to make clear which port has been called by which vessel, we will indicate (A) or (B) after each port and after each seavoyage. The results of the measurements in port are shown in Table 2.

Table 2: Concentrations in port in μg.m^{-3}.{exposure time in hours}.

IN PORT	Zone	Port of Wilhelmshaven (B) {15 h}	Port of Kotka (B) {108 h}	Port of Rotterdam (B) {11 h}	Port of Rotterdam (A) {24 h}	Port of Rauma (A) {33 h}	Port of Hamina (A) {52 h}
benzene	AC	5.01	2.06	62.1	–	–	–
	ER	3.10	16.5	75.4	–	–	–
	Gsz	6.88	1.92	76.4	–	–	–
	Gdz	2.45	1.50	58.9	–	–	–
toluene	AC	16.1	7.49	14.2	99.3	75.6	–
	ER	13.4	55.1	20.9	277	69.1	25.6
	Gsz	22.4	6.99	14.7	101	78.7	–
	Gdz	39.0	159	86.2	935	80.3	–
m+p-xylene	AC	15.8	7.37	10.5	85.7	70.0	18.6
	ER	15.2	76.0	22.7	324	1550	78.7
	Gsz	24.5	7.59	10.8	104	56.8	15.3
	Gdz	6.46	46.2	2.93	932	73.2	–
o-xylene	AC	6.28	1.87	4.41	55.4	23.8	–
	ER	5.86	23.6	9.56	275	314	13.6
	Gsz	9.63	1.73	4.58	57.8	18.5	–
	Gdz	2.58	1.13	1.53	418	25.4	–
ethylbenzene	AC	12.2	2.43	7.55	17.9	23.5	–
	ER	11.3	51.8	17.2	173	309	22.7
	Gsz	19.1	2.41	9.41	38.3	20.6	–
	Gdz	5.10	1.19	2.54	811	31.6	–
1,3,5-TMB	AC	3.98	0.857	2.55	–	–	–
	ER	3.69	16.0	6.12	68.5	45.6	20.0
	Gsz	6.22	0.736	2.41	12.8	–	–
	Gdz	1.13	0.247	0.376	270	6.86	–
1,2,4-TMB	AC	12.6	2.89	8.41	77.7	38.5	18.9
	ER	12.2	52.0	20.0	435	293	123
	Gsz	19.6	2.45	7.10	47.8	21.9	9.51
	Gdz	2.90	0.767	1.11	1794	53.0	–

(– = below the detection limit)

The benzene concentrations for ship A were all found to be below the detection limit.

Sea voyage

The results of the measurements at sea are displayed in Table 3. The benzene concentrations for ship A were all found below the detection limit except for two measurements in the AC at sea, location AC 0. Although some of the transported products might contain a small amount of benzene, its vapour is not detectable in our measurements.

Table 3: Concentrations at sea in μg.m^{-3} {exposure time in hours}.

AT SEA	Zone	Seavoyage Rotterdam Wilhelmshaven (B) {19h}	Seavoyage Wilhelmshaven Kotka (B) {76h}	Seavoyage Kotka Rotterdam (B) {93h}	Seavoyage Rotterdam Rauma (A) {93h}	Seavoyage Rauma Hamina (A) {33h}
Benzene	AC	2.21	3.27	2.10	3.27	1.65
	ER	2.52	22.1	9.72	–	–
	Gsz	1.59	1.94	1.49	–	–
	Gdz	–	1.18	1.26	–	–
toluene	AC	7.75	7.85	4.71	16.9	291
	ER	10.3	41.7	33.0	11.3	608
	Gsz	6.81	6.80	6.31	13.5	471
	Gdz	74.4	338	343	58.4	385
m+p-xylene	AC	6.49	12.7	3.56	44.8	86.9
	ER	9.99	38.1	40.2	109	261
	Gsz	5.92	4.34	3.88	39.5	141
	Gdz	3.11	7.80	6.26	531	157
o-xylene	AC	2.62	7.70	2.31	4.36	1.30
	ER	3.77	11.9	13.3	23.9	49.8
	Gsz	2.18	1.64	1.39	12.2	34.5
	Gdz	1.28	2.34	1.43	178	32.9
ethylbenzene	AC	3.47	5.83	1.88	7.51	22.8
	ER	6.78	33.4	23.4	22.5	56.7
	Gsz	3.29	2.92	2.29	15.4	27.3
	Gdz	0.211	2.65	1.99	191	43.2
1,3,5-TMB	AC	1.05	2.84	0.970	3.55	15.3
	ER	2.15	6.56	9.18	11.5	37.9
	Gsz	0.944	1.02	0.926	3.55	16.7
	Gdz	–	0.301	0.369	30.8	20.0
1,2,4-TMB	AC	3.49	8.53	3.28	21.8	85.4
	ER	7.55	20.0	29.5	72.5	250
	Gsz	3.06	3.27	3.05	16.9	103

(– = below the detection limit)

The results for benzene on ship B reflect a concentration below or near to the detection limit. Two exceptions are the ER during the voyage from Wilhelmshaven to Kotka (B) and from Kotka to Rotterdam (B).

DISCUSSION

During normal cargo operations some cargo vapours are released into the atmosphere. These vapours should be traceable in the gdz. What we wanted to investigate is whether traces of these cargo vapours can also be found in other areas on board of the vessel. The first zone that has been evaluated is the gsz.

A comparison between the gsz and the gdz

In order to compare both zones, the (gdz/gsz) ratio will be used. We will first discuss the results ship by ship, and draw up a conclusion later by comparing both results.

Ship A

Ship A transported cargoes whereof the vapours had a direct influence on our measurements, namely toluene, xylene, solvesso 100 (34 wt% 1,2,4-TMB). As a general result for this vessel, we found that the concentration in the gdz exceeded the concentration in the gsz. Exceptions to this rule are the port of Hamina and the toluene and o-xylene concentration between Rauma and Hamina. This is shown in Table 4.

Table 4: Concentration ratios for the gdz to the gsz for ship A

Ratio gdz/gsz	Benzene	Toluene	m+p-Xylene	o-Xylene	Ethyl - benzene	1,3,5-TMB	1,2,4-TMB
Port of R'dam (A)	*	9.2	9.0	7.2	21	21	37
Sea voyage R'dam-Rauma (A)	*	4.3	13	15	12	8.6	13
Port of Rauma (A)	*	1.0	1.3	1.4	1.5	*	2.4
Sea voyage Rauma-Hamina (A)	*	0.8	1.1	0.9	1.5	1.1	1.2
Port of Hamina (A)	*	*	0.0	*	*	*	0.0

* indicates that the concentration in the gsz equals 0

From table 4 we learn that in Rotterdam and during the voyage from Rotterdam to Rauma the gdz/gsz ratio was situated well above unity, while in Rauma and during the voyage from Rauma to Hamina the same ratio was close to one, or even smaller than one. For both ports, the relative wind direction was the same, abeam from starboard, and therefore this parameter cannot be responsible for the difference. The major reason is the fact that during loading operations a considerable amount of cargo vapours are released on deck (gdz > gsz), while during discharging operations this is considerably less or even nil (gdz $\cong$ gsz). When loading, the ship's tank is filled up, and consequently the pressure inside the tank will rise. At a preset pressure the relief valve will evacuate the tank vapours at a speed of 30 m.s^{-1} into the atmosphere of the gdz. Thanks to the true wind coming in from the starboard side, most of the vapours were evacuated to the portside, and not into the gsz. This resulted in Rotterdam in an important difference in concentrations between the gdz and the gsz. When discharging, the ship's tank is emptied, and a negative pressure is created inside the tank. The vacuum valve will at a preset negative pressure open, and allow air into the tank to partially fill up the vacuum. During this operation no cargo vapours will escape from the tank and therefore the influence of the cargo on our measurements in Rauma is rather small.

Comparing both sea voyages is more difficult. The voyage from Rotterdam to Rauma was a laden voyage. Due to ship movements small amounts of toluene, xylene and 1,2,4-TMB vapours were released in the gdz. We noticed that only fractions from these concentrations were measured in the other zones. This is illustrated in Figure 3.

The voyage from Rauma to Hamina was a voyage with extensive tank cleaning and tank ventilation. Considerable amounts of toluene, xylene and 1,2,4-TMB vapours have been ventilated into the gdz. We expected here also a greater value in the gdz compared to the gsz. But the results in Figure 4 clearly show that the concentration in both zones is almost equal or even a little bit higher in the gsz. As we definitely know that the main sources here are the tanks, we conclude that the ventilated cargo vapours entered the gsz, and even show a tendency to accumulate there. Accordingly the concentration in the 3 other zones is remarkably higher than during the previous voyage.

Another exception is the port of Hamina. As can be found in Table 2, all values from both zones are close to the detection limit, reducing the significance of the gdz/gsz ratio. The reason why the concentrations here are situated near the detection limit can be explained by the fact that all cargoes with a direct influence on the measurements have been discharged and cleaned earlier and the fact that there is only little industrial activity in Hamina.

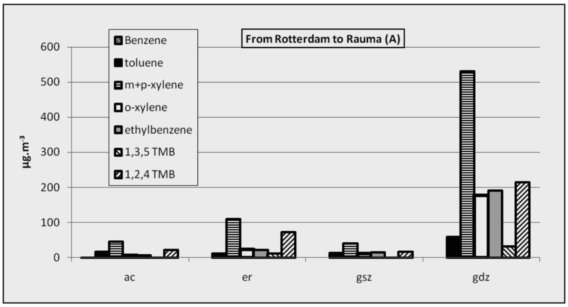

Figure 3: Concentrations in µg.m^{-3} for the different zones from Rotterdam to Rauma, ship A.

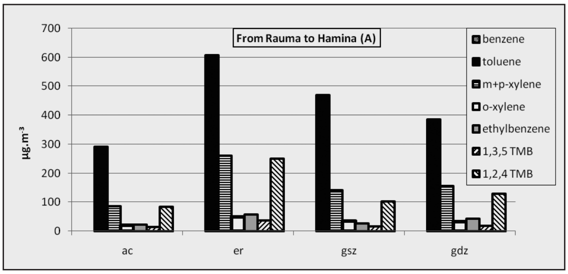

Figure 4: Concentrations in µg.mm^{-3} for the different zones from Rauma to Hamina, ship A.

Ship B

For ship B none of the transported cargoes did have a direct influence on the measurements. While on ship A in general gdz concentrations exceeded the gsz ones, we found on ship B the opposite. Exceptions were the toluene and the m+p-xylene concentrations in Kotka. These results are shown in Table 5. Also for the o-xylene concentrations for Wilhelmshaven to Kotka and for Kotka to Rotterdam, the gdz value exceed those of the gsz. But since the absolute concentrations are very low, varying from 1.39 to 2.34 μg.m^{-3} (see Table 2), we found this less relevant.

Table 5: Concentration ratios for the gdz to the gsz for ship B

Ratio gdz/gsz	Benzene	Toluene	m+p-Xylene	o-Xylene	Ethyl - benzene	1,3,5-TMB	1,2,4-TMB
Seavoyage R'dam-W'haven(B)	0.0	10.9	0.5	0.6	0.1	0.0	0.1
Port of W'haven(B)	0.4	1.7	0.3	0.3	0.3	0.2	0.1
Seavoyage W'haven-Kotka(B)	0.6	49.7	1.8	1.4	0.9	0.3	0.3
Port of Kotka(B)	0.8	22.8	6.1	0.7	0.5	0.3	0.3
Seavoyage Kotka-R'dam(B)	0.8	54.3	1.6	1.0	0.9	0.4	0.4
Port of R'dam(B)	0.8	5.8	0.3	0.3	0.3	0.2	0.2

The ratio clearly shows a toluene pollution source situated in the gdz. Unlike ship A, no toluene cargo was on board of this ship. However we found an intermediate bulk container (IBC) on deck, containing approximately 1 m^3 of toluene. This toluene is sometimes used for tank cleaning purposes. An inspection of this IBC taught us that the container was not gastight closed as the cap was broken. In this way toluene vapours were released continuously, explaining the relatively high concentrations for toluene in the gdz. The IBC was situated within 10 meter distance from our sampler. This situation looks very similar to the laden voyage of ship A, where only the sampler near the facing showed an increased concentration for the products transported. The higher m+p-xylene ratio in Kotka was due to an increased gdz value. An explanation for this increment has not been found.

In contrast with ship A, the gdz/gsz ratio on ship B is in general below 1. And although the absolute concentrations for ship B are lower, it is a contradiction that the gdz shows lower concentrations than the gsz. This was definitely not the intention of the IBC code. The ratio indicates that the major source is closer to or situated in the gsz.

Evaluation of the ER

The results found on ship B in the gsz were expected to be lower compared to the gdz. However, the concentrations in the ER of ship B are the highest of all four zones on the exception of toluene in the gdz. May we consider the ER as the major voc source on board of ship B? In order to confirm this statement, we calculated the indoor/outdoor (I/O) ratio for the ER. This ratio is shown in Table 6.

In most cases the ratio is well above 1 in spite of the powerful mechanical ventilation present in the ER. The I/O ratio is in most cases above unit, indicating that the engine room itself is the major source and the ventilation here is insufficient or inefficient. The I/O ratio is only in two locations below unit, namely in Wilhelmshaven and for benzene in Rotterdam. The results in Wilhelmshaven are appar-

Table 6: Indoor/outdoor ratio in the ER for ship B.

I/O ER	Benzene	Toluene	Ethyl - benzene	m+p-Xylene	o-Xylene	1,3,5-TMB	1,2,4-TMB
R'dam/W'haven	1.6	1.6	2.2	2.0	2.0	2.7	3.1
W'haven	0.3	0.5	0.4	0.5	0.5	0.5	0.5
W'haven/Kotka	11.3	4.9	11	7.4	6.3	6.3	6.0
Kotka	11	9.0	50	16	19	467	42
Kotka/R'dam	4.8	3.1	6.1	6.3	5.9	5.8	5.7
R'dam	0.8	2.3	2.7	3.6	3.2	4.9	5.3

ently influenced by pollution from outside since the main engine is not running. The toluene/benzene ratio in Table 7 confirms that both compounds are coming from the same source, except of course for the facing where the sampler has been influenced by the small amounts of toluene escaping from the IBC. The presence of the coal driven power plant nearby might be the main cause for this outdoor pollution.

Table 7: Toluene - benzene ratio in Wilhelmshaven

AC 0	AC bridge	inlet AC	inlet ER	Facing
3.3	3.1	3.2	3.2	16

In Rotterdam we measured unexpectedly high benzene concentrations at all samplers, indicating that the whole ship was "covered" by a same level of benzene vapours. As there was no benzene cargo on board, and as never before such high concentrations of benzene have been measured on board, it seems obvious that this pollution came from shore.

Besides these two cases where the atmosphere around the vessel has been under influence of shore pollution, we find on ship B an I/O ratio for the ER (well) above 1. Regretfully we could not make the same comparison for ship A as the results for inlet ER ship A were disturbed by an excessive air flow from the ER ventilation.

Based on the results of ship B we conclude that in the ER important pollution sources are present. Further detailed research in the ER is necessary in order to identify these sources.

Positioning of the ventilation inlets

As we measured quite a difference in absolute concentrations between the ventilation inlet of the AC and the ventilation inlet of the ER, we tried to determine which of both inlets was located best. Both concentrations are only available for ship B, as the concentrations near the inlet ER on ship A were rejected due to a too high ventilation speed. The results for ship B are shown in Table 8.

Both ventilation intakes are somewhat 20 meters apart. But more important is the fact that the AC intake is situated about 8 meters higher than the ER intake. The latter is situated 4 m more aft and on the starboard side. This is the side where we placed our sampler and it is the intake which is most frequently used. The AC

Table 8: Ratio inlet AC/inlet ER for the different compounds and different measuring periods with the corresponding wind direction and wind force on board of ship B.

Position	Benzene	Toluene	Ethyl-benzene	m+p-Xylene	o-Xylene	1,3,5-TMB	1,2,4-TMB	Rel. wind direction	Rel. wind force
Kotka	1.5	1.3	3.7	2.2	1.7	3.2	3.0	110 SB	2
R'dam	0.7	2.3	1.9	2.5	2.1	2.9	2.8	160 PS	3
W'haven	0.5	0.5	0.5	0.6	0.6	0.6	0.6	60 SB	3
Kotka/ R'dam	0.5	0.2	0.2	0.2	0.2	0.2	0.2	25 PS	4
R'dam/W'haven	1.0	1.1	1.1	1.4	1.3	1.4	1.5	155 PS	4
W'haven/Kotka	1.0	0.6	0.9	0.7	0.7	0.9	1.0	20 SB	3

intake is situated on the portside. From Table 8 we learn that there is a direct relation between the ratio inlet AC/inlet ER and the relative wind direction. When this relative wind is forward of the beam or ahead, we noticed that the ratio is smaller than 1. If on the other hand, the relative wind is coming in from a direction abaft the beam or from astern, the ratio is found to be above 1. We have seen before that the influence of the cargo on our measurements on board of this vessel is rather small. The exhaust gases from the main engine and the auxiliaries together with possible shore pollution in port can be considered as the major sources. This is in agreement with the relative position of both inlets compared to the position of the funnel. In terms of percentage, a wind from forward of the beam has a higher frequency of occurrence than a wind from abaft the beam, due to the ship's speed. Therefore we may conclude that the position of the AC inlet is a better choice, although not ideal in all circumstances. One exception on the above described relation is the benzene concentration in Rotterdam. This is a confirmation of a previous conclusion, namely that in Rotterdam a shore benzene pollution influenced our measurements. The concentrations near the AC inlet were clearly lower than near the ER room inlet. In view of the difference in height, the relative vapour density of benzene (2.7) is a possible explanation. So the result in Wilhelmshaven where also shore pollution was considered could be explained by this same reason.

Evaluation of the AC

An interesting space to discuss more in detail is the AC. The result of the samplers placed inside the AC, one at level 0, and one at the bridge level, should give an answer to the question whether cargo vapours are traceable in the ER.

As shown in Table 9, there is a good correlation between the results of level 0 and the bridge level concentrations on ship A. This correlation is somewhat lower for m+p-xylene, although both locations have the same ventilation inlet. Moreover the absolute concentrations at level 0 were always found to be greater than the bridge level concentrations. Opening and closing of doors for deck access at level 1 is a possibility for an increased concentration.

Table 9: Pearson correlation between samplers at AC level 0 and bridge level on board of ship A.

Toluene	Ethylbenzene	M+p-Xylene	o- Xylene	1,3,5-TMB	1,2,4-TMB
0.995	0.950	0.821	0.973	0.991	0.984

Table 10: Indoor/outdoor ratio for AC on board of ship A.

I/O AC	Benzene	Toluene	Ethyl - benzene	m+p- Xylene	o-Xylene	1,3,5- TMB	1,2,4- TMB
R'dam		1.0	0.9	0.8	1.0	0.0	1.6
R'dam/Rauma		2.5	1.0	1.1	1.1	1.0	1.3
Rauma		1.0	1.1	1.2	1.3	*	1.7
Rauma/Hamina		0.6	0.8	0.6	0.6	0.9	0.8
Hamina		*	*	1.2	*	*	2.0

*outdoor concentration equals 0

The presence of cargo vapours in the AC is visible in the indoor/outdoor ratios of Table 10. As expected, the indoor/outdoor ratio in Rotterdam is below unit, due to the local pollution outside. However an exception is 1,2,4-TMB. But when we keep in mind that Solvesso 100 has been loaded in Antwerp only 14 hours ago, it is possible that remnants of this operation are still present inside the AC, resulting in a relatively high ratio. Once at sea, we would expect lower concentrations outside and thus a ratio above unit. This is particularly the case for the cargo related vapours, toluene, xylene and 1,2,4-TMB. This is another indication that cargo vapours entered the AC during the stay in Rotterdam. In Rauma the concentrations at the AC inlet hardly differ from the inlet concentrations at sea, except for toluene. This means that the air quality in Rauma is almost as good as at sea, resulting in an indoor/outdoor ratio equal to or above unity. When we started cleaning and venting the tanks on the way to Hamina, the ratios decreased below one. As can be concluded from Table 10, particularly the vapours related to the transported cargoes show a lower ratio, proving that cargo vapours arrived at the ventilation inlet of the AC . Finally we arrived in Hamina with all toluene, xylene and Solvesso 100 tanks cleaned and made gas free. And as the industrial activity in Hamina is rather low, the ratios became again above unity, at least for these results where the measured concentrations were above the detection limit.

The results of the bridge sampler and the level 0 sampler on ship B are strongly correlated as shown in Table 11. Both have the same ventilation intake, and we do not expect different sources for both spaces. The indoor/outdoor ratio shown in Table 12 teaches us that in general on ship B this ratio is below unity in port, above unity at sea. This is an understandable result, as we may consider the air at sea to be less polluted compared to the air in port. This statement is somewhat less evident for the benzene concentration indicating the presence of a benzene source or accumulation inside. The relatively high percentage of smoking crewmembers might be responsible for that result.

Table 11: Pearson correlation between the samplers at AC level 0 and at the bridge level on ship B.

correlation AC-bridge	Benzene	Toluene	Ethyl - benzene	m+p- Xylene	o-Xylene	1,3,5- TMB	1,2,4- TMB
	1.000	0.978	0.991	0.974	0.993	0.981	0.957

Table 12: Indoor/outdoor ratio for AC on board of ship B.

I/O AC	Benzene	Toluene	Ethyl - benzene	m+p- Xylene	o-Xylene	1,3,5- TMB	1,2,4- TMB
R'dam/W'haven	1.3	1.1	1.0	0.9	0.9	0.9	0.9
W'haven	1.1	1.1	0.9	0.8	0.8	0.8	0.8
W'haven/Kotka	1.7	1.5	2.0	3.6	3.1	2.9	2.7
Kotka	0.9	0.9	0.6	0.7	0.8	0.8	0.8
Kotka/R'dam	1.7	2.4	2.5	2.5	2.4	3.5	3.4
R'dam	1.0	0.7	0.6	0.7	0.7	0.7	0.8

From the AC indoor/outdoor ratio on ship A and ship B we learned that in some particular cases, cargo vapours do enter the AC, that generally spoken in port the concentration indoor is below outdoor concentration, and that at sea it is just the other way around. Particularly cleaning and venting of cargo tanks leads to increased outdoor concentrations, and as a consequence also to increased indoor concentrations. The ideal would be if we could fully isolate the AC from all toxic vapours outside. This is of course hypothetical as the crew needs access to the deck part. Naval architects have thought about a solution to have access to deck without vapours from outside entering the AC. This is called the 'crew changing room'. It is a small compartment situated at level 1 on the starboard side, with a door on one side giving access to the AC, on the other side a door giving access to the main deck. This compartment acts as an air lock. According to the ventilation plan, this room has a ventilation capacity of $400m^3.h^{-1}$ resulting in 27 air changes per hour. Another use of this compartment is that the crew changes their workclothes used outside, with clothes for indoor use and leaves the used clothes also in this compartment in order to bring them later to the laundry. As it is realistic that in this space higher concentrations could occur, we placed on ship B an extra sampler and the results are shown in Figure 5. Some peak values can be found in this figure. Especially the sea voyages Wilhelmshaven to Kotka and Kotka to Rotter-

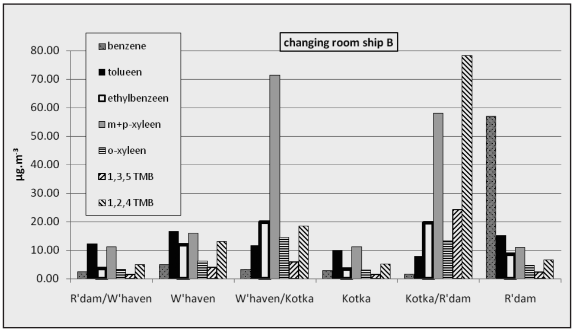

Figure 5: Concentrations in the changing room of ship B.

dam draw our attention. The ethylbenzene, xylenes and 1,2,4-TMB concentrations were significantly higher. In an attempt to find out whether all compounds are originating from the same source, Table 13 shows ratios between the analyzed compounds and respectively toluene and benzene. Toluene and benzene concentrations are related to another source, at least for the two above mentioned voyages.

Although the ventilation in the changing room is completely separated from the ventilation in the AC, we will compare both concentrations. The sampler placed in the AC on level 0 is located somewhat 8 meters away from the changing room. Any differences in concentrations between the two samplers are most probably in relation with the quality of the supplied air. The correlation between both concentrations over the whole measuring campaign is shown in Table 14. This correlation confirms the conclusion from Table 13. For benzene and toluene there is a good to even perfect correlation.

For the other compounds there is no correlation at all, confirming that these results were influenced by a different source. When we compare the absolute concentrations of the AC level 0 and the absolute concentration in the changing room for those compounds that do not show any correlation, the changing room concentrations are during 2 seavoyages definitely higher, namely from Wilhelmshaven to Kotka and from Kotka to Rotterdam. During these two voyages the ratio changing room over AC level 0 varies between 1.8 and 18. There is a source of ethylbenzene, xylenes and trimethylbenzene present in the changing room. As none of these products were related to the cargo, the source must be different. A first possibility is cigarette smoke from the duty mess nearby. But a further study of the ventilation plan showed a very surpris-

Table 13: Ratios for the measured compounds to toluene and benzene in the changing room on ship B.

Compound ratios in changing room	Benzene/ toluene	Ethyl-benzene/ toluene	m+p-Xylene/ toluene	o-Xylene/ toluene	1,3,5-TMB/ toluene	1,2,4-TMB/ toluene	Ethyl-benzene/ benzene	m+p-Xylene/ benzene	o-Xylene/ benzene	1,3,5-TMB/ benzene	1,2,4-TMB/ benzene
R'dam/W'haven	0.2	0.3	0.9	0.3	0.1	0.4	1.5	4.6	1.3	0.6	2.0
W'haven	0.3	0.7	1.0	0.4	0.2	0.8	2.4	3.3	1.3	0.8	2.6
W'haven/Kotka	0.3	1.7	6.2	1.2	0.5	1.6	6.0	21.9	4.4	1.8	5.6
Kotka	0.3	0.3	1.1	0.3	0.2	0.5	1.2	4.0	1.1	0.6	1.9
Kotka/R'dam	0.2	2.5	7.4	1.7	3.1	9.9	12	37	8.4	15	49
R'dam	3.7	0.6	0.7	0.3	0.1	0.4	0.2	0.2	0.1	0.0	0.1

Table 14: Pearson correlation between the concentrations measured in the AC and in the changing room on ship B.

Correlation between the AC and changing room	Benzene	Toluene	Ethyl - benzene	m+p-Xylene	o-Xylene	1,3,5-TMB	1,2,4-TMB
	1.000	0.979	0.102	-0.090	-0.007	-0.246	-0.255

Figure 6: Positioning of inlet changing room relative to vent polluted water tank and thermal oil tank.

ing result. The intake of the supply of the changing room is situated just above the vents of the polluted water tank and thermal oil tank, as shown in Figure 6. The polluted water tank contains a mix of water and all kinds of other liquids that cannot be discharged directly because of ecological reasons. These liquids are temporarily stored in the polluted water tank for decantation. Examples of other liquids are bilges water or liquids from any leak in the ER. It is not uncommon that these liquids contain hydrocarbons. In order to accelerate the segregation/decantation with water, this tank is kept at a temperature between 50°C and 70°C. Therefore it is not surprising that different compounds do have a higher concentration in the changing room. We would therefore advice the crew not to use the supply for the changing room, but only the extraction fan. Our results show that the air in the gdz is cleaner than the air near the polluted water tank vent. This error in the configuration of the ventilation raises some doubts whether naval architects are really concerned about the seafarers' health.

CONCLUSIONS

Comparing ship A with ship B shows that the cargo has a very important influence on the absolute concentrations. During most of the cargo handling the influence of cargo vapours is restricted to the gdz, but when loading and especially during cleaning and ventilating the tanks, the cargo vapours can be found all over the vessel. A second important pollution source is the ER. Although the absolute concentrations found are well below these of the cargo, the results clearly show that there is a problem in the ER despite the mechanical ventilation. A third pollution source, depending on the location, is the shore. The loading and discharging operations mostly take place in an industrial area, and sometimes really close to the production or treatment plant. The example given of the crew changing room ventilation arises the doubt whether naval architects are sufficiently concerned about the seafarers' health. Our conclusion is that the actual ventilation configuration can be improved.

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