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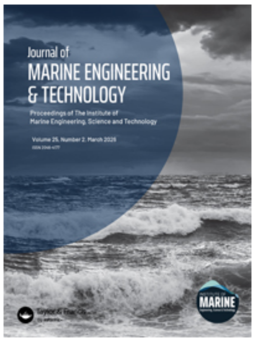

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Salinity and volatile organic compounds in engine room air of a sea-going vessel

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ABSTRACT

Introducing polymer electrolyte membrane fuel cells (PEMFCs) in vessels is a viable way to accomplish zero-emission shipping. However, PEMFC performance can degrade due to intrusion of airborne contaminants via the cathode inlet. This study focuses on salt and the VOCs benzene, toluene and naphthalene specifically. Little to no data is available on their concentration inside engine rooms of sea-going vessels because on board measurements have not been conducted or reported. Especially for air salinity, experimental contamination concentrations might be significantly higher than the salt in sea air. Therefore, field-measurements were conducted on board of a ship in various weather conditions and at different locations on Western European sea routes. The average saline concentration was 4.3×10^{-3} µg/L with a maximum of 2.0×10^{-2} µg/L inside the ship. The highest measured value is 4.2×10^{5} times lower than the average concentration applied in experimental literature. This suggests further degradation studies are needed to clarify the impact of lower, representative amounts of salt on PEMFCs performance. Benzene, toluene and naphthalene remained at least one order of magnitude below harmful concentrations and are therefore not expected to cause degradation in maritime fuel cells.

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Maritime; PEMFCs; degradation; field-measurements; NaCl; VOC

Abbreviations

AST =	Accelerated stress test
F.O.C =	Fuel oil consumption
PEMFC =	Polymer electrolyte membrane fuel cell
SSA =	Sea spray aerosols
SD =	Standard deviation
VOC =	Volatile organic compound

1. Introduction

Developing sustainably-powered ships is essential to reach the goals of the Paris agreement. The maritime industry emits about 3% of the greenhouse gas emissions, a percentage that will only increase if no action is taken (IMO 2020; DNV 2023). Replacing fossil fuelled energy systems with polymer electrolyte fuel cells (PEMFCs) is one of the promising solutions. When running on sustainable hydrogen, they are free from harmful emissions. Compared to other fuel cells, PEMFCs run at low temperature, can operate dynamically, start up quickly and have a high power density (Baroutaji et al. 2016). However, PEMFC durability is still a bottleneck and pollutants in marine air might cause performance loss. Literature shows that, among others, volatile organic compounds (VOCs) (Moore et al. 2000; Thampan et al. 2006; Li H et al. 2009; Angelo et al. 2010; Angelo and St-Pierre 2014; St-Pierre et al. 2014; Wang et al. 2014; Misz et al. 2016; Reshetenko and St-Pierre 2016; Shabani et al. 2019; St-Pierre and Zhai 2020; Viitakangas et al. 2020; Schmid et al. 2022) and sodium chloride (NaCl) (Mikkola et al. 2007; Steinbach et al. 2007; Lee et al. 2011; Uemura et al. 2017; Kitahara and Nakajima 2018; Nakajima et al. 2019; Lamard et al. 2022; Park et al. 2022; Lamard et al. 2023; Briand et al. 2024, 2025) intrusion via the air inlet could have a detrimental effect the PEMFC performance. Unfortunately, there is no data on their concentration in engine room air. It is essential to have representative engine room air concentrations to assess if PEMFCs can tolerate the contaminants or if the design must be adapted to clean the air.

Ship's engine rooms are ventilated with marine air, which is fed to the PEMFCs cathode. For the salinity, the salt concentrations of seas and oceans around the world are known, but the concentration in air or engine rooms is rarely discussed in literature. The MARANDA project recently investigated the impact of air salinity on humidifiers on board of ships (Tallgren and Ihonen 2018). The authors used a reference value of $10\,\mu/m^3$ salt in unfiltered sea air. However, they did not provide details on how the value was derived and under what conditions it is representative. This makes it hard to verify if the reference value is suitable for saline degradation tests in PEMFCs. VOCs originate from many processes including (burning of) fossil fuels, evaporation from solvents and reforming of hydrocarbons. It is unknown at which quantities these remain in the engine rooms or to what extent they are taken in from surrounding air into the ships.

The PEMFC sea salt tolerance is challenging to pin down. Only Briand et al. (2024) test with values close to sea air concentrations. Various other saline contamination experiments have been done, in which saline air is generally generated by nebulising saline solutions. It is not possible to directly compare the experimental outcomes, as various factors influence the contamination level and thus the extent of damage. The most important factors are the concentration of the saline solution, the air and water flow rate and the surface area of the membrane electrode assembly. The data in the literature can be used to derive an area specific salt flow in g/h/cm^2, so that the contamination flow rate and electrode surface area are included and experimental campaigns can be compared.[1] In published experiments, the average area specific salt flow is 1.8×10^{-2} g/h/cm^2 NaCl

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(Mikkola et al. 2007; Steinbach et al. 2007; Uemura et al. 2017; Kitahara and Nakajima 2018; Nakajima et al. 2019; Lamard et al. 2022; Park et al. 2022; Lamard et al. 2023; Briand et al. 2024; 2025).

Most studies use NaCl, as it makes up 85% to 90% of sea salt (Lenntech 2023). These experimentally tested area specific contaminant flows are nearly six orders of magnitude[2] higher than the value assumed in the MARANDA project (Tallgren and Ihonen 2018). One explanation could be that the experiments are accelerated stress tests (ASTs) in which the contamination level is increased to observe effect in a shorter period of time and with less interference of other degradation mechanisms. Another reason is that salt might accumulate in the PEMFC, as maritime systems are expected to last ten-thousands of hours. Still, the discrepancy between experiments and MARANDA seems excessive. For VOCs, especially benzene, naphthalene and toluene have been studied in PEMFCs, at concentrations ranging from 0.25 to 50 ppm (Shabani et al. 2019; Zhao et al. 2020; Schmid et al. 2022). Section 2.2 elaborates on the tolerance levels. In summary, multiple publications look into the effect of NaCl and VOC contamination, yet it is unclear what concentrations can be expected in engine rooms.

The aim of this study is to obtain reference values for the amount of salt and VOCs that maritime PEMFCs will be exposed to. We conducted field-measurements on board a sea-going vessel. Samples were collected at three locations on board during the voyage in various weather conditions. Section 1 provides more information on how salt enters and exits the air, how to measure air salinity, and VOC sources and sampling procedures. In Section 2 more details of the set-up are given. In Section 3 we compare our findings with contamination concentrations from literature and suggest directions for maritime PEMFC degradation research.

2. Background

2.1. Air salinity sources, impact and sampling

Salt is present in the sea air in the form of sea spray aerosols (SSAs). Their diameter varies, but the majority of the aerosols have a diameter $<1\ \mu\mathrm{m}$ at a relative humidity of 80% (de Leeuw et al. 2011). Particles inside the SSAs are suspended in air and consist mostly of sea water droplets and dry sea salt particles (Lewis and Schwartz 2004). Even though both dissolved and solid salts are carried in the air, the majority of the salt is present in dissolved form (de Leeuw et al. 2011).

SSAs are mostly generated from whitecaps – the white areas of the sea surface where sea water and air bubbles are mixed together. When the air bubbles burst, the watery outer layer disintegrates into drops which are injected into the atmosphere (Lewis and Schwartz 2004; de Leeuw et al. 2011). At high wind speeds (>10 m/s), the wind can tear sea water drops off of wave crests without the need for bursting of bubbles (Monahan et al. 1982; de Leeuw et al. 2011).

Salt is removed from the air via deposition. The two main mechanisms are dry deposition due to the pull of gravity, in which coagulation between salt particles increases deposition speed, and wet deposition, in which precipitation washes the salt particles from the air (de Leeuw et al. 2011).

Clearly, many factors influence the salt concentration in the air. Wind speed is one of the most important factors as it impacts the amount of air that is mixed in the water, the uptake of salt from wave crests, and deposition (Lewis and Schwartz 2004). Yet, other factors also play a role including temperature, water salinity, wave types and rainfall. For a ship, conditions inside are different from outside, the temperature and wind speeds differ and part of the particles likely deposit on the air-intake structures such as fans or grates. This will likely result in different air salinity values inside the engine room compared to the outside air. For that reason field-measurements should be taken both in the engine room as well as outside.

Aqueous salinity measurements are more common and easier to conduct compared to measurements in air. The former are based on electric conductivity, acoustic waves or even optical refraction indexes (Gu et al. 2022), while the latter require a different approach. The majority of the publications on atmospheric techniques are from meteorological literature. The techniques include membrane sampling (Lovett 1978; Lewis and Schwartz 2004; He et al. 2018; Jiang et al. 2021), high resolution photography (Lewis and Schwartz 2004), flame photometry (Clark et al. 2001; Campuzano-Jost et al. 2003) and differential mobility analysis (Intra and Tippayawong 2008).

If salt contaminants reach sufficiently high concentrations, they can be harmful for PEMFCs. NaCl crystals, as well as Na^+ and Cl^- ions can cause different kinds of harm. Various publications, including the work of Li S et al. (2025) and our recent review (Broer et al. 2025), discuss the mechanisms and impact of salt contamination in more detail.

2.2. VOC sources, impact and sampling

VOCs are a broad group of chemicals, but this study only considers three: benzene, toluene and naphthalene, as these have shown to reduce output voltage in earlier PEMFC studies. They can originate from fossil fuels and internal combustion engines, as benzene, toluene and naphthalene are released through sublimination from or combustion of gasoline, diesel, oil and coal (Moore et al. 2000; Misz et al. 2016; Reshetenko and St-Pierre 2016). Therefore, it is fair to assume the VOCs could pose a risk for PEMFC powered vehicles when they sail in highly industrialised areas, alongside main shipping routes with fossil-powered ships, or when PEMFCs are combined with an internal combustion engine in the same power train. The latter will be common because hybrid configurations with fuel cells and fossil fuel based generators are expected to be common in the initial phase of the maritime energy transition (DNV 2022).

VOCs decrease PEMFC performance by binding to the catalyst sites, reducing the surface area available for the reduction of O_2. Tables 1–3 provide an overview of the VOC contamination experiments. The aim of overview is to find experimental PEMFC tolerance limits for benzene, toluene, and naphthalene. Note that contaminant mixtures have a more complex interaction, and can either have a stronger or a less severe effect on performance degradation (Jing et al. 2007; Angelo and St-Pierre 2014; Qi et al. 2019). To the best of our knowledge, there is no work that considers the combined impact of benzene, toluene and naphthalene. Therefore, the paragraphs below address the studies that work with single contaminants only.

Benzene contamination studies (Table 1) show that it matters whether the contaminant enters via the anode or cathode inlet. Thampan et al. (2006) introduced 20 ppm benzene via the anode for 100 h and Wang et al. (2014) conducted a similar experiment with 10 ppm benzene. Both authors concluded that there were no signs of significant degradation. In contrast, studies in which benzene is introduced via the cathode inlet (i.e. the air inlet) do report signs of performance decay. Moore et al. (2000) observed a reduction of 28% in the cell potential when operating at $0.2\ \mathrm{A/cm^2}$ for 30 minutes with 50 ppm benzene contamination. Angelo and St-Pierre (2014) and Reshetenko and St-Pierre (2016) measured significant potential decay as well, when operating on lower contamination levels of 2 ppm. Interestingly, the current density has a strong impact on the voltage reduction. At higher current densities, the voltage drop increases (Moore et al. 2000; Angelo and St-Pierre 2014; Reshetenko and St-Pierre 2016). This is a relevant finding to keep in mind when

Table 1. Benzene literature findings.

Reference	Cell	Contam. (ppm)	Insertion (an/cath)	Duration (hours)	Findings
Moore et al. (2000)	Single cell	50	Cath	0.5 h	5% V reduction at 0.05 A/cm^2 and 28% V reduction at 0.2 A/cm^2. Recovery after 1 min OCV and operation on clean air.
Thampan et al. (2006)	Single cell	20	An	100 h	No signs of degradation
Angelo and St-Pierre (2014)	Single cell	2	Cath	20 h	Voltage drop 200 mV at 1.0 A/cm^2, lower (about 50 mV) at 0.2 A/cm^2 In contaminant mixtures with SO2 and NO2, performance loss greater than the sum of performance losses induced by the individual contaminants
Wang et al. (2014)	Single cell	10	An	$>$ 100 h	At 1 A/cm^2 voltage loss rate increased from 62.3 to 89.8 μV h^{-1} Authors claim no significant impact of benzene
Reshetenko and St-Pierre (2016)	Segmented cell	2	Cath	30 h	Loss of 40–45 and 100–110 mV at 0.2 and 1.0 A/cm^2 respectively. At 0.2 A/cm^2 mostly inlet MEA affected, at 1.0 A/cm^2 outlet showed higher losses.

Table 2. Toluene literature findings.

Reference	Cell	Contam. (ppm)	Insertion (an/cath)	Duration (hours)	Findings
Thampan et al. (2006)	Single cell	20	An	100 h	No signs of degradation. Exhaust gas analysis shows 90% of toluene is converted to methylcyclohexane.
Li H et al. (2009)	Single cell	1–50	Cath	ca. 200 h	Significant voltage drop, also at 1 ppm. Loss is higher with increasing contaminant concentration, increased air stoichiometry and higher current. Mainly charge transfer losses increase.
Angelo et al. (2010)	Single cell	2	An	$>$ 100 h	No signs of degradation. Exhaust gas analysis shows 100% of toluene is converted to methylcyclohexane.
Lee et al. (2011)	Single cell	0.1–5 ppm	Cath	10–20 h	Stronger voltage drop with higher air stoichiometry, higher toluene centration, or higher current density. Increasing the relative humidity results in lower voltage degradation.
Wang et al. (2014)	Single cell	20	An	$>$ 100 h	At 1 A/cm^2 voltage loss rate increased from 40.8 to 63.7 μV h^{-1}. Authors conclude toluene has no significant impact on degradation.
St-Pierre et al. (2014)	Single cell	20	Cath	0.9–1.9 h	At 1 A/cm^2, 45°C and humidified air, strong voltage drop of $>$ 80% within one hour. With dry air a similar result after 1.9h. 5th most harmful out of 21 tested contaminants.
Misz et al. (2016)	Single cell	0.1–3	Cath	1 h	Degradation increases with lower temperature and higher voltage. 0.1 ppm only slight effect, 1 ppm causes 15% current drop in potentiostatic mode at 0.7 V and 87°C. At 70°C even stronger current drop and worse regeneration
Viitakangas et al. (2020)	5 cell stack	10–50 ppm, 0.5 ppm CO	An	4 h	Negligible effects of 10 and 20 ppm, 50 ppm toluene caused 37 to $>$ 50 mV drop compared to 5 mV drop in reference. 50 ppm toluene in combination with 0.5 ppm CO smaller overall effect than sum of individual contamination tests.
Schmid et al. (2022)	5 cell stack	0.15–0.25	Cath	5–7 days	Lower catalyst loading results in higher degradation rate. 150 ppb causes V decay, at a rate of 32 to 65 μV h^{-1} at catalyst loading of 0.1 and 0.4 mg/cm^2 respectively.

Table 3. Naphthalene literature findings.

Reference	Cell	Contam. (ppm)	Insertion (an/cath)	Duration (hours)	Findings
St-Pierre et al. (2014)	Single cell	20	Cath	$<$ 1 h	Most harmful out of 21 tested contaminants. Both with and without humidification, voltage dropped below 20%. No recovery when operating on clean air.
Reshetenko and St-Pierre (2016)	Segmented cell	2.3	Cath	10 h	Performance loss of 0.53 V (80%) within 9 h. Normalised current density increased at the inlet and decreased at the outlet. Recovery possible after 2h operation on clean air.
St-Pierre and Zhai (2020)	5 cell stack	1.4	Cath	10 h	Test with normal and low catalyst loading. At 0.4 mgPt/cm^2 voltage drop of 26% due to increase in kinetic and mass transfer resistance. Full recovery possible. At 0.1 mgPt/cm^2 rapid decline and no recovery.

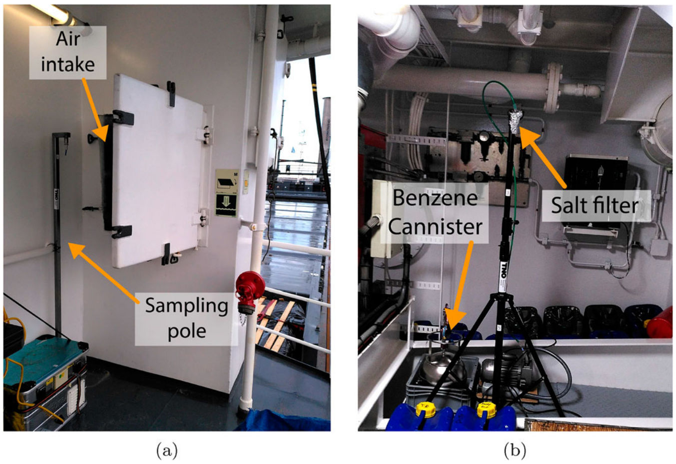
accessing VOC degradation experiments. Probably PEMFCs will be operated towards high current densities, as that is the region with the highest power density (Zhang 2008).

Similar to benzene contamination, experimental studies introducing 2–20 ppm *toluene* via the anode show limited to no effect on the cell potential (Thampan et al. 2006; Angelo et al. 2010; Wang et al. 2014; Viitakangas et al. 2020). Viitakangas et al. (2020) did show that higher concentrations of 50 ppm could be harmful. This risk increases when anode gas recirculation is applied, as is often the case in commercial systems, because it allows impurities to accumulate. Still, the cathode seems to be more sensitive, and small amounts of toluene can cause a significant voltage drop as shown in Table 2. Schmid et al. (2022) showed that 0.15 ppm toluene already resulted in a degradation rate of 65 μV h^{-1}. Slightly higher concentrations of 1 ppm resulted in 5% voltage drop (Li H et al. 2009) or 15% current drop (Misz et al. 2016). Degradation increases with higher toluene concentration, current density or air stoichiometry and reduces with higher temperature or catalyst loading (Li H et al. 2009; Lee et al. 2011; St-Pierre et al. 2014; Misz et al. 2016; Schmid et al. 2022). Both benzene and toluene contaminated cells recover when running on clean air, preceded by an OCV phase in case of high contaminant concentration (Moore et al. 2000; St-Pierre et al. 2014; Reshetenko and St-Pierre 2016; Shabani et al. 2019). This indicates the degradation is reversible.

Lastly, *naphthalene* seems to be more harmful than benzene (Reshetenko and St-Pierre 2016) or toluene (St-Pierre et al. 2014) in comparative studies. Literature results are shown in Table 3. In work by St-Pierre et al. (2014), 20 ppm of the VOC caused a voltage drop of over 80% within an hour. Recovery was not possible afterwards, meaning the damage was irreversible. Lower concentrations of 1.4 and 2.3 ppm cause voltage drops as well, although it could be restored after operation on clean air (Reshetenko and St-Pierre 2016; St-Pierre and Zhai 2020). Results from the same authors show that performance probably only degrades 1% over the fuel cell lifetime if naphthalene exposure remains below 0.2 ppm (St-Pierre et al. 2013). However, these outcomes are generated by a mathematical model that needs further experimental validation.

Even though the voltage loss is often recoverable by operation with clean air (St-Pierre et al. 2014; Shabani et al. 2019; Zhao et al. 2020), fuel cell operators do not control the air quality and thus clean air might not be available. This might be harmful especially in maritime applications, where a drop in power output can lead to high safety risks. Therefore, performance degradation can better be avoided, and contaminants in the airflow should remain below the tolerance level. Judging from Tables 1–3 these tolerance levels are 2, 0.15 and 1.4 ppm for benzene, toluene and naphthalene respectively. If needed, air filters can reduce contaminant levels. This does come at a cost, as filter systems can be bulky and expensive, especially if the air needs to be cleaned to a high purity (IMPELL Purification Technologies LP 2024). The system becomes less efficient as more energy is required to overcome the pressure loss over the filter (Subrenat et al. 2000). In addition, the filters themselves need to be replaced periodically, increasing the maintenance costs. To balance system size and costs with contamination risk, maritime engineers should know the VOC concentration in engine room air to decide if and to what extent filtration is needed.

VOC concentrations can be determined by field studies. Samples can be taken with solid absorbents, that pre-concentrate the chemicals, or with Tedlar bags or stainless steel canisters to store the air itself (Wilbur et al. 2007). In both cases, the samples should be analyzed in a laboratory environment to obtain the concentration.



(a) (b)

Figure 1. NaCl sampling set-up (a) outside sampling pole, shielded from rain, and (b) inside the engine room port side. The starboard-side set-up inside the engine room not shown.

3. Method

3.1. Sampling membranes and canisters

A membrane-pump combination was used for air salinity samples while VOC samples were taken using stainless steel canisters. Membrane salt sampling was preferred over other methods as it is affordable and easy to conduct, in contrast to flame photometry and differential mobility analysis. This enabled the ships' crew to conduct sampling with minimal training. High resolution photography gives more insight into particle size distribution rather than the salt concentration in the air and was therefore less relevant.

Three sampling set-ups were installed on board of the ship (Figure 1), one starboard outside, and two inside the engine room, on port side and starboard respectively. The outside set-up was shielded from the rain and located at 20 cm from the engine room air inlet. For each set-up the membrane was fixed on a pillar 1.5 m above the floor and a canister was placed on the floor. The hosting ship was a general cargo vessel named the 'Ankie', measuring 90 by 12.5 m, operated by Van Dam Shipping.

The vessel sailed to various routes in the Baltic Sea, North Sea, Bay of Biscay and Mediterranean Sea. Maps of the exact sample locations are shown in Figure 2 (NaCl) and Figure 3 (VOCs). A total of nine salt samples was taken in four different conditions: (1) two samples in a harbour independent of weather conditions; (2) one sample at sea while it rained regardless the wind speed; (3) three samples at sea with dry weather and wind speeds <5 m/s; and (4) three samples at sea with dry weather and wind speeds >10 m/s. The number of samples in each condition was based on chance, depending on stable weather conditions and availability of the set-up operator. The sampling time was at least 2 h up to 24 h. Longer duration was preferred, yet sampling was stopped if environmental conditions changed, so that a sample remained representative of the weather condition. After completion of the sample, the membrane was detached and stored in a protective case. VOC samples were collected in two different conditions: (1) in harbour environments and (2) at open sea, two in each condition. Each took 2 h to complete, after which the canisters were closed and stored inside.

3.2. Determining benzene and salt concentrations

Both the membrane samples and VOC canisters were sent off for analysis by an external party (Environmental Modelling, Sensing and Analysis department of Netherlands Organisation for Applied

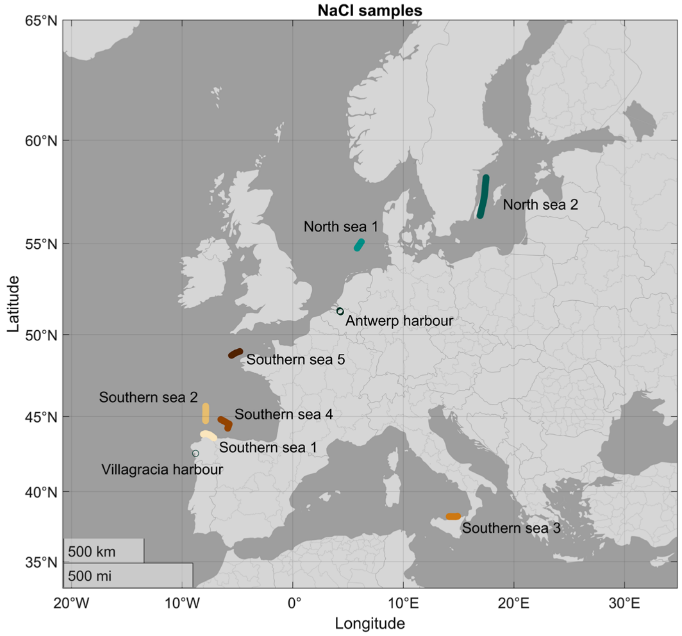


Figure 2. Salt sample locations.

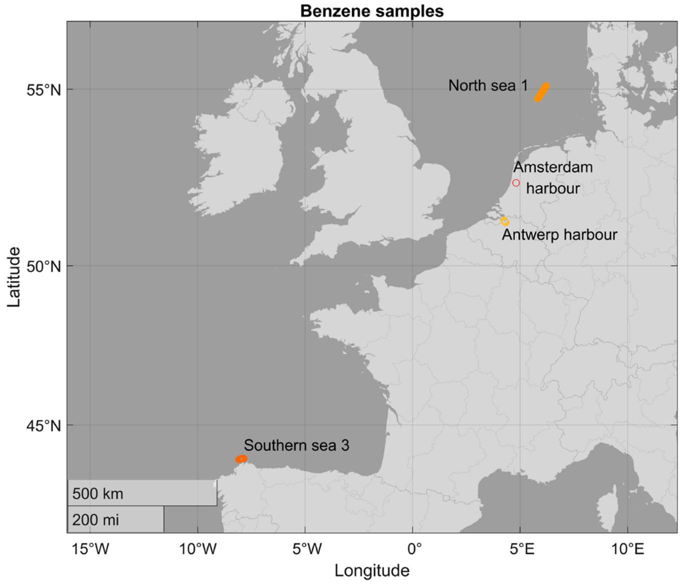


Figure 3. Benzene sample locations.

Table 4. Averaged wind and engine data during measurements.

Location	Wind speed (m/s) [SD*]	Average F.O.C.* (kg/h) [SD*]	Tag
North Sea 1	3.20 [1.1]	110.0 [76.7]	SN1.W−.D
Antwerp harbour	7.36 [2.5]	217.6 [2.2]	HAntw
Southern sea 1	1.83 [1.9]	0 [0]	SS1.W−.D
Villagracia harbour	2.25 [1.2]	67.0 [8.1]	HVil
Southern sea 2 S*	10.46 [5.6]	250.1 [3.3]	SS2.W+.D
Southern sea 2 V*	3.05 [0.9]	79.5 [13.3]	SS2.W−.D
Amsterdam harbour	1.46 [0.6]	0 [0]	HAmst
Northern sea 2	4.99 [2.2]	165.6 [8.6]	SN2.W−.D
Southern sea 3	9.54 [2.8]	196.9 [5.4]	SS3.W+.D
Southern sea 4	16.66 [3.8]	139.5 [11.3]	SS4.W+.D
Southern sea 5	11.01 [1.3]	231.4 [1.6]	SS5.W+.W

Note: *SD = standarddeviation; F.O.C. = fueloilconsumption; S = During NaCl sampling period (> 14 h); V = During VOC sampling period (2 h)
Note that F.O.C of the main engine is shown.

Scientific Research). The salt within the sampling membranes was dissolved in desalinated water. Because potassium ions can also compose 0.5% to 1.2% of the ions in sea salt, they were also measured. The chloride concentrations were determined via ion chromatography while an inductively coupled plasma mass spectrometer (ICP-MS) was used to measure the sodium and potassium concentrations. The lower detection limits for Na^+, K^+ and Cl^- were < 1111, < 1 and < 1111 µg/filter respectively.

$$C_{air.ug/L} = \frac{ion_{fltr}}{t\Delta_{sample} * Q_{pump}} \tag{1}$$

was used to convert the ion amount per filter (ion_{fltr} in µg/filter) to the salt concentration in the air ($C_{air,ug/L}$ in µg/L). Here $t\Delta_{sample}$ is the sampling time in minutes, which varied from 120 to 1200 minutes (2.5 to 20 h), and Q_{pump} is the airflow pumped through the membrane, varying from 8.2 to 8.4 L/min. Equation (A1) in the supporting information describes this unit conversion in more detail. For further analysis, the three ion concentrations were added together to an accumulated salt concentration in µg/L. This facilitates the comparison between the measured data and experimentally applied concentrations, as the latter are also accumulated values.

VOC air samples were prepared with thermal desorption and thereafter analysed via gas chromatography and mass spectrometry (TD-GCMS). Reported concentrations were calculated according to the TO15 standard with a lower detection limit of $<1\,\mu/\mathrm{m}^3$ (i.e. $<3.1 \times 10^{-4}$ ppm). A total of 22 chemicals were screened, including benzene, toluene and naphthalene. To convert the laboratory data from μ/m^3 to ppm we applied

$$C_{VOCppm} = \frac{C_{lab} * V_m}{M_{VOC}}. \tag{2}$$

Here C_{VOCppm} is the concentration of the VOC in ppm, C_{lab} the concentration of the VOC in ambient air as provided by the lab in μ/m^3, V_m the molar volume of an ideal gas (i.e. $2.446 \times 10^{-2}\,\mathrm{m}^3/\mathrm{mol}$ at 1 bar and 25°C), and M_{VOC} the molar mass of the VOC in g/mol. Equation (A2) in the supporting information section shows a more detailed derivation of this unit conversion equation.

4. Results and discussion

Table 4 provides context for the salt (Section 4.1) and benzene (Section 4.2) results. It shows the location, averaged wind speed, and average fuel oil consumption of the main engine during sampling. Beside these factors, sea salinity, and precipitation also have an impact on air salinity. For that reason Table 4 has a descriptive sample tag in the right-most column. The location is indicated by SN (Northern Sea, including the Baltic Sea and North Sea) or SS (Southern sea including the Bay of Biscay and the Mediterranean Sea); the wind speed by W− (< 5 m/s) or W+ (wind > 10 m/s); and precipitation by D (dry weather) or R (rain). Harbours were tagged as HVil (Villagracia), HAmst (Amsterdam) and HAntw (Antwerp).

4.1. *Salt concentrations vastly lower than experiments and vary strongly*

Figure 4 plots the accumulated salt concentration (sum of Na^+, K^+ and Cl^- inos) at each location together with the horizontal blue line representing the MARANDA reference (Tallgren and Ihonen 2018). It is apparent that salt concentrations vary significantly. The lowest measurement, taken inside the engine room, was $6.9 \times 10^{-4}\,\mu\mathrm{g\,L}^{-1}$ while the highest concentration was $5.1 \times 10^{-1}\,\mu\mathrm{g\,L}^{-1}$ measured outside.

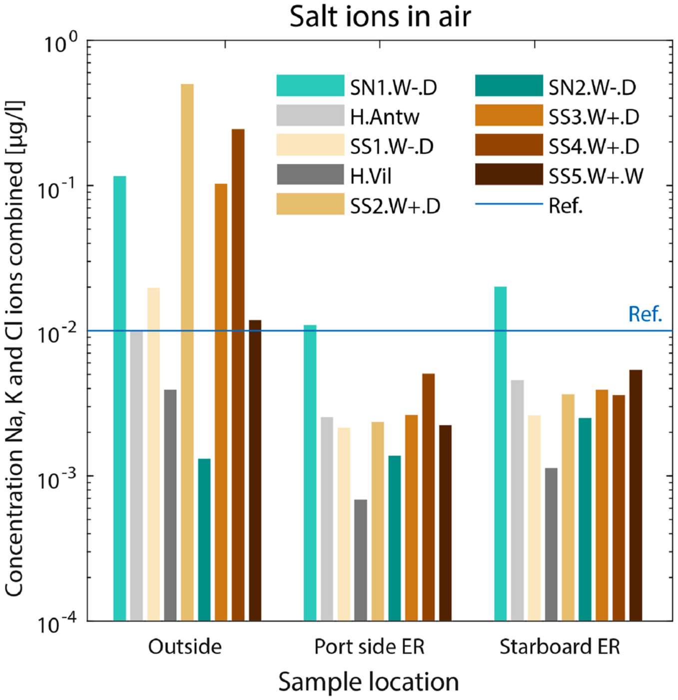


Figure 4. Combined concentration of Na, K and Cl ions from different sample positions (outside, port side engine room, starboard engine room) and at nine different conditions. Reference line shows the concentration reported in the MARANDA project (Tallgren and Ihonen 2018). ER on the x-axis refers to engine room.

In line with our expectations, concentrations outside are higher than inside with averages of 1.1×10^{-1} and 4.3×10^{-3} µg/L respectively. The port side and starboard concentrations are similar to one another, suggesting the air salinity is evenly distributed in the engine room. The MARANDA reference corresponds quite well to the highest values measured inside the engine room. This implies that experimental literature on air salinity degradation indeed used substantially higher concentrations compared to those present in engine room air (Mikkola et al. 2007; Steinbach et al. 2007; Uemura et al. 2017; Kitahara and Nakajima 2018; Nakajima et al. 2019; Lamard et al. 2022; Park et al. 2022; Lamard et al. 2023; Briand et al. 2024, 2025).

Even when taking the highest engine room value (SN1.W−.D at starboard, 0.0202 µg/L), and normalising it to the maximum airflow of a commercial PEMFC system, it is still 4.2×10^5 times lower than the average value scholars applied in experiments so far.[3] Ships require power systems with long lifetimes, thus cumulative exposure could still cause issues. Yet, there is no proof that salt will accumulate at low concentration exposure. In the recent study by Briand et al. (2025), salt is clearly found in PEMFC effluent. Even if all salt would accumulate, the average experiment still introduced two orders of magnitude more salt compared to reality. Therefore, the current literature gives insight in possible degradation mechanisms, but the reported damage is probably unrealistically high.

The outside samples indicate that the air in harbour areas (H.Antw and H.Vil in Figure 4) contains less salt compared to air at sea. This seems plausible because at sea, no matter from which direction the wind is blowing, it can pick up more SSA from the sea surface. Based on the theory in Section 2.1, air salinity should be low in Northern Seas, when it rains and with little wind, and it should be high in Southern Seas, when it is dry and when the wind is blowing hard. For example, samples with high wind conditions and dry weather at the southern sea (SS2.W+.D, SS3.W+.D and SS4.W+.D) resulted in high outside air salinity.

Nonetheless, a couple of samples do not match the weather conditions theory. For instance the second sample at the Northern Seas (SN2.W−.D), which had the lowest salt concentration while the weather was dry. It is especially puzzling that sample SN1.W−.D, taken in similar weather conditions, showed to be one of the highest recorded concentrations, even though the wind speed was lower than for SN2.W−.D. Partially, this lack of alignment with theory follows from taking data in an uncontrolled environment, rather than in laboratories. The wind direction could be another factor of importance. The wind sensor used in this study was supposed to give wind-direction data as well. However, during data analysis, the operator indicated that the sensor had been located in a rather wind-shielded location (Hasselaar 2025). On average, sampled values slightly underestimate wind speed, as shown in the supplementary information Section A.4. Because this study aims to get a reference for engine room air salinity, and air salinity increases with wind speed, the potential higher actual wind speed samples are still considered relevant. The wind direction data, that was recorded as well to support analysis, has been disregarded as the offset was too large to consider data useful.

A final interesting observation is that high air salinity outside does not always result in high concentrations inside. For instance, the outside sample of SS2.W+.D is 5.0×10^{-1} µg/L higher than the average of the two inside values. Samples SN1.W−.D, SS3.W+.D and SS4.W+.D also show a large discrepancy between outside and inside values of 1.0×10^{-1}, 1.0×10^{-1} and 2.4×10^{-1} µg/L respectively. This could be related to the relative wind direction as well, especially given that the ventilation shafts are opened towards the aft of the ship. Less salt is expected to infiltrate the ER if the wind blows from bow to aft compared to it being directed from aft to bow.

Questions remain regarding conditions influencing the outside air salinity, and the relation between outside and inside concentrations. In order to understand the data in depth, further research would be required. More samples should be taken to obtain significant results, at multiple locations and more factors, such as wind direction and even higher wind speeds, should be considered in the sampling set-up. However, for the sake of this study, in which we aim to obtain a reference value for PEMFC contamination levels, the current data is sufficient.

4.2. Higher VOC concentrations inside, yet far below harmful threshold

The VOC concentrations at the three sample locations are shown in Figure 5. All measurements stay far below harmful values for PEMFCs. As concluded in Section 2.2, benzene, toluene and naphthalene are shown to reduce fuel cell performance when they exceed 2, 0.15 and 1.4 ppm respectively. The highest measurement in this campaign was 0.02 ppm of toluene. Risks of PEMFC contamination by VOCs is therefore deemed very unlikely.

Clearly, VOC concentrations are higher inside the engine room than outside. Outside, half of the naphthalene, and 75% of the benzene samples were below the detection limit. Even in the industrialised Amsterdam harbour, the outside VOC concentration was very low (for toluene, Figure 5B) or below the detection limit (for benzene and naphthalene, Figure 5A,C). Inside the VOC concentrations are higher and distributed unevenly. The VOCs source or sources are most likely located on the starboard side of the engine room. The fuel oil consumption in Table 4 correlates with use of the ship's engine. The table shows that little to no fuel is consumed at H.Amst and SN1.W−.D, while values in Figure 5 are high (dark blue and dark yellow bars). One explanation for this is that when the engine consumes more fuel, it runs at higher power. It will also draw in more air, possibly diluting the VOC concentration. In order to validate this

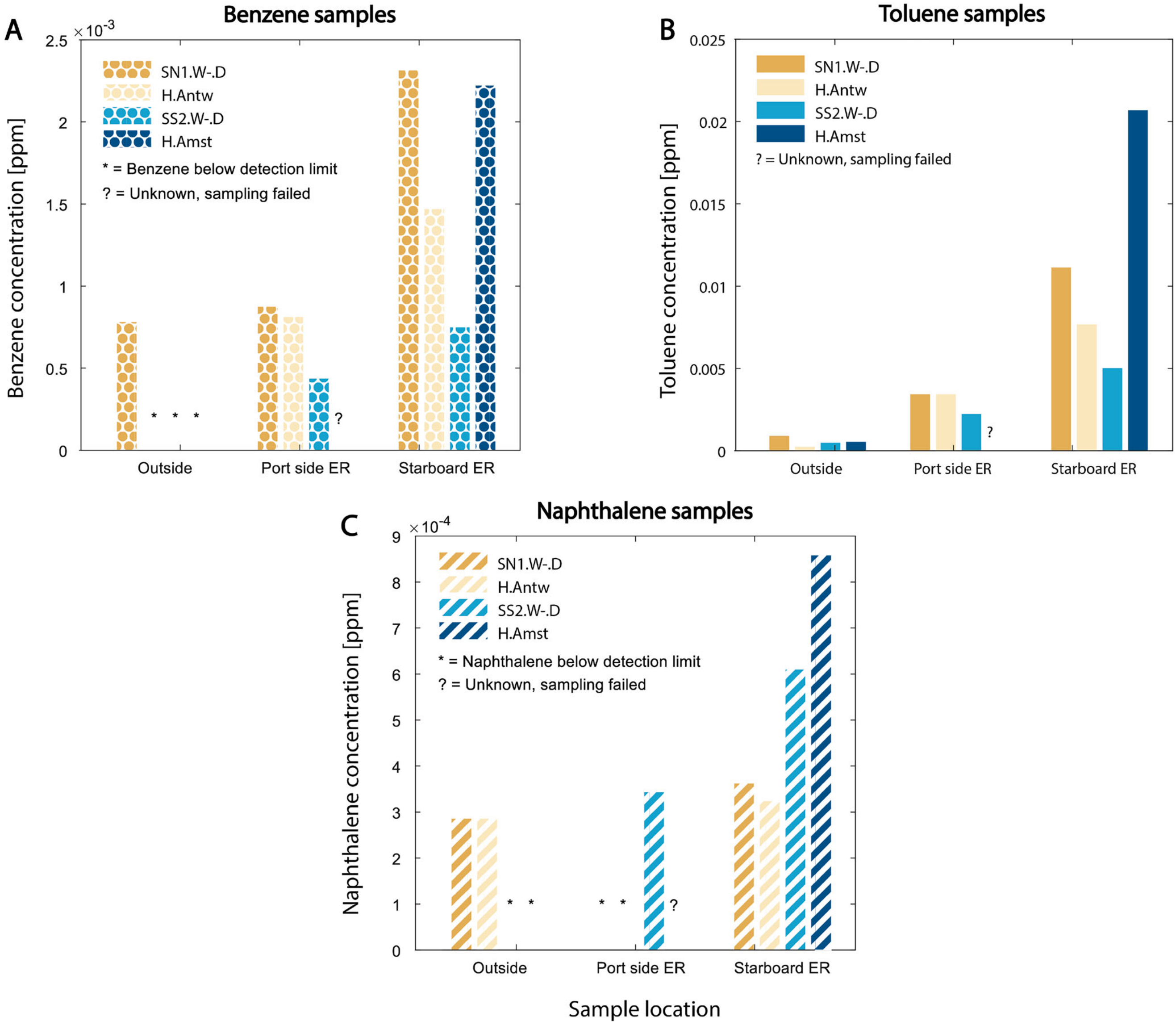


Figure 5. VOC concentrations of benzene (A), toluene (B) and naphthalene (C). The samples were taken at different positions on board (outside, port side engine room, starboard engine room) at four geographical locations (SN – Northern sea; H.Antw – Antwerp harbour; SS – Southern sea; H.Amst - Amsterdam harbour). ER on the x-axis refers to engine room.

hypothesis, more samples should be taken to see if the pattern holds. Yet, the current study only aims to find if VOCs could pose a threat to maritime PEMFCs, and more detailed research is thus outside the scope of the current study.

5. Conclusion – implications for maritime PEMFC research

This study aimed to find reference values for engine room air contamination in ships, as data on VOC and NaCl air concentrations is not available in literature. Representative reference values are essential to improve maritime PEMFC degradation tests. During field measurement on board of a vessel, samples were taken both outside and in the engine room. Values of $4.3 \times 10^{-3}\ \mu\mathrm{g\,L^{-1}}$ (average) and $2.0 \times 10^{-2}\ \mu\mathrm{g\,L^{-1}}$ (highest) are representative for the engine room air salinity of this campaign. These results suggest salt concentrations in experimental work are often significantly higher than actual sea air. On average, PEMFC degradation studies apply concentrations five orders of magnitude higher than our highest inside measurement. More specifically, the SN1.W−.D starboard value is 4.2×10^{5} times lower than the average NaCl concentration applied in experimental studies. Therefore, the current salinity literature mainly aids in understanding possible degradation mechanisms, as none of them test with realistic air salinity values. Additional experimental research is required to understand the relation between air salt concentration and degradation, to discover if there is an air salinity level that PEMFCs can tolerate, and to determine suitable mitigation strategies for maritime PEMFCs.

The salt samples indicate that concentrations vary widely. Environmental conditions such as the sea salinity, wind speed and precipitation seem to impact the air salinity, although they cannot fully explain all results. Possibly wind direction has an impact, although further research is required to explore this hypothesis.

Despite the fact that PEMFCs are sensitive to benzene, toluene and naphthalene in air, the data from this campaign shows that the VOCs remain at least one order of magnitude below harmful values. The highest occur at the starboard side of the engine room, 2.3×10^{-3}, 2.1×10^{-2} and 8.6×10^{-4} ppm for benzene, toluene and naphthalene respectively. VOC concentrations are larger inside engine rooms, outside they were often below the detection limit. This implies that benzene, toluene and naphthalene contamination will most likely not degrade maritime fuel cells performance.

In conclusion, this provides a valuable dataset and analysis of air quality inside engine rooms. Results give insight into realistic contamination levels, which aid in engineering reliable and affordable PEMFC systems for sea going vessels. By doing so, the current work contributes to development of maritime PEMFC systems and, in extension, to zero-emission shipping.

Notes

1. All conversion calculations are reported in the supporting information
2. Check equation A5 in the supporting information to see how we computed the commercial area specific salt flow using the MARANDA value and assuming a current density of 1 A/cm^2 and an air stoichiometry of 2.
3. See section A.2.2 in the supporting information for detailed conversion steps. The area specific salt flows of literature studies are provided in section A.3 and are part of our recently published review (Broer et al. 2025)

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Disclosure statement

We have no conflicts of interest to disclose. We confirm that this work is original and has not been published elsewhere, nor is it under revision for publication elsewhere. While under consideration, this work will not be submitted to any other journal.

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