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Characterization of scrubber water discharges from ships using comprehensive suspect screening strategies based on GC-APCI-HRMS

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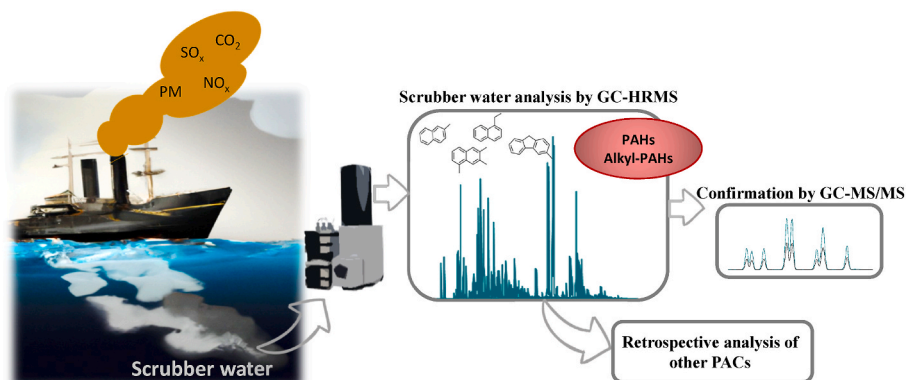
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HIGHLIGHTS

- Exhaustive suspect screening for contaminants identification was applied.
- Higher level of compound identification was achieved by GC-MS/MS.
- Naphthalene, Phenanthrene and alkyl homologues are the most frequent in scrubbers.
- Retrospective analysis was used to identify other polycyclic aromatic compounds (PACs).
- PAHs, alkyl-PAHs, and PACs are relevant markers of scrubber water contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

An extended suspect screening approach for the comprehensive chemical characterization of scrubber discharge waters from exhaust gas cleaning systems (EGCSs), used to reduce atmospheric shipping emissions of sulphur oxides, was developed. The suspect screening was based on gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) and focused on the identification of polycyclic aromatic hydrocarbons (PAHs) and their alkylated derivatives (alkyl-PAHs), which are among the most frequent and potentially toxic organic contaminants detected in these matrices. Although alkyl-PAHs can be even more abundant than parent compounds, information regarding their occurrence in scrubber waters is scarce. For compound identification, an in-house compound database was built, with 26 suspect groups, including 25 parent PAHs and 23 alkyl-PAH homologues. With this approach, 7 PAHs and 12 clusters of alkyl-PAHs were tentatively identified, whose occurrence was finally confirmed by target analysis using GC coupled with tandem mass spectrometry (GC-MS/MS). Finally, a retrospective analysis was performed to identify other relevant (poly)cyclic aromatic compounds

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(PACs) of potential concern in scrubber waters. According to it, 18 suspect groups were tentatively identified, including biphenyls, dibenzofurans, dibenzothiophenes and oxygenated PAHs derivatives. All these compounds could be used as relevant markers of scrubber water contamination in heavy traffic marine areas and be considered as potential stressors when evaluating scrubber water toxicity.

1. Introduction

Shipping has long been recognized as an energy-efficient mode of transport medium for moving freight (Corbett, 2003). Nevertheless, combustion in ship engines produces a range of primary and secondary pollutants (i.e., those formed in the atmosphere) such as, particulate matter (PM), carbon dioxide (CO₂), sulphur oxides (SO_x), nitrogen oxide (NO_x) and ozone (O₃) and contributes significantly to their emission to the atmosphere. To mitigate the impact of SO_x (and indirectly PM) emissions from shipping, the International Maritime Organization (IMO) has reduced the global maximum sulphur content in marine fuels from 3.5% to 0.5% m/m (mass by mass) (Resolution MEPC.32074, 2019). Naturally occurring low sulphur fuel is scarce and desulphurization in refineries is expensive, leading to higher prices of compliant low-sulphur fuels. Thus, many shipping companies have chosen to install exhaust gas cleaning systems, also known as scrubber systems, on their vessels and thereby reach compliance, still using high-sulphur residual fuels.

During the scrubbing process, the exhaust gas is driven through a fine spray of water which readily dissolves sulphur oxides so that levels are sufficiently reduced in air emissions (Turner et al., 2017). However, the waste stream generated, known as scrubber water, is a toxic chemical cocktail discharged into the marine environment (Tran, 2017). There are two types of scrubbers, open and closed loop. The open-loop discharges the entire wash water volume back to the sea while the closed-loop releases smaller volumes, but with higher concentration of pollutants as the wash water is recirculated in the scrubbing process (Lunde Hermansson et al., 2021). Although there are now thousands of ships equipped with scrubbers, there is still little information on the potential environmental risks associated with the discharge of scrubber water. Some studies already pointed out that contaminants such as polycyclic aromatic hydrocarbons (PAHs) and metals are frequent pollutants in scrubber water (Lunde Hermansson et al., 2021). Besides the parent PAHs, the alkylated derivatives of PAHs are also expected to be of relevance and present at even higher concentrations than their parent compounds. PAHs are organic pollutants of great concern due to their potential carcinogenic and mutagenic properties (IARC Monographs, 1987), and there is evidence that alkyl-PAHs can be even more toxic than parent PAHs (Lam et al., 2018; Sun et al., 2014; Vondráček et al., 2007). This is especially the case for alkyl-PAHs with 3–5 rings, which have been identified as the main components of oil toxicity to aquatic organisms (Hodson et al., 2007). The number of studies that evaluated the effects of scrubber water discharges to marine organisms are still limited and, in most cases, they only focused on the 16 priority PAHs as the major contributors to the toxicity, excluding the alkylated derivatives (Koski et al., 2017; Ytreberg et al., 2019). Thus, to assess the environmental and human health risks associated with scrubber water discharges, a comprehensive chemical characterization of scrubber water is necessary to identify the most relevant alkyl-PAHs derivatives, together with other compounds of interest.

Gas chromatography (GC) is the most common technique for the identification of volatile, thermally stable, and non-polar organic micropollutants. However, GC-MS and GC-MS/MS target methods are limited to the analysis of a restricted number of pre-determined compounds, overlooking the occurrence of other relevant components. In this way, untargeted techniques, such as those based on high-resolution mass spectrometry (HRMS), and quadrupole-time-of-flight (QTOF), allow acquiring huge amount of chemical information in a single analysis (de Boer and Law, 2003; Poster et al., 2006). When using GC-HRMS instruments, soft ionization techniques, such as Atmospheric Pressure

Chemical Ionization (APCI), are mostly used. These ionization sources have lower fragmentation potential and often provide higher intensities for molecular ions, and/or the protonated molecule, thus facilitating the identification of the contaminants (Carrasco-Pancorbo et al., 2009; Portolés et al., 2010, 2014; Wachsmuth et al., 2011). Another advantage of using HRMS based techniques is their potential for retrieving information on the occurrence of other relevant organic contaminants in the samples, at any time, through retrospective analysis which means that, the data can be re-examined for other contaminants not included in the first screening, without the need for further analysis (Campos-Mañas et al., 2019; Gago-Ferrero et al., 2015; Portolés et al., 2010). Even though GC-APCI-HRMS has been widely used in both target and untargeted analytical applications (Niu et al., 2020), to the best of our knowledge, this is the first time that this technique is used for the identification of alkyl-PAHs derivatives in scrubber water samples.

In this study, a comprehensive chemical characterization of scrubber waters was performed to identify the most relevant non-polar organic contaminants that could be considered as markers of scrubber water contamination in marine ecosystems. To accomplish this objective, samples produced in a pilot scrubber system were first analyzed by GC-APCI-QTOF-MS, using a comprehensive suspect screening strategy to identify the most relevant alkyl-PAHs homologues. The occurrence of the identified compounds was further confirmed by target analysis using GC-MS/MS. Finally, other potentially relevant contaminants derived from the scrubber water, that can be potential contributors to its toxicity were also identified by means of a comprehensive retrospective analysis.

2. Materials and methods

2.1. Chemicals and reagents

Mixtures of 16 priority PAHs and isotopically labelled standards for PAHs were purchased from AccuStandard (Connecticut, EE. UU) and Dr. Ehrenstorfer (Augsburg, Germany), respectively. In the case of the alkyl-PAHs, they were acquired from Chiron Laboratory (Norway), Dr. Ehrenstorfer (Augsburg, Germany) and Toronto Research Chemicals (Ontario, Canada). More details can be found in the supplementary material.

2.2. Pilot scrubber system and generation of scrubber water

The scrubber water was produced by a pilot-scale engine lab at the Department of Mechanics and Maritime Sciences, Chalmers University of Technology. The lab is equipped with a four-cylinder 100 kW engine from Volvo Penta and a scrubber unit made of stainless steel holding a length of 50 cm and a diameter of 40 cm. The scrubbing process was carried out by pumping seawater to the scrubber unit through 7 different nozzles (BETE, Micro Whirl MW105) to create an adequate mist. The water flow rate was kept at 1 L min⁻¹ yielding a water-to-air ratio of 0.0006 inside the scrubber unit. This is a slightly lower water-to-air ratio compared with that recorded in onboard measurements (Fridell and Salo, 2016) who observed a water-to-air ratio of 0.004 in roll-on roll-off on-board measurements in vessels. The engine ran on 0.8% sulphur marine gas oil at approximately 25% engine load and the produced exhausts were led to the scrubber unit using a vacuum pump. The engine exhaust flow rate was monitored using a mass flow meter (TSI, Mass Flowmeter 4000 Series) and was kept at 1.7 m³ min⁻¹.

The scrubber system was operated in two consecutive series with two different seawater samples as inlet water, which was collected at 32 m

depth at Kristineberg Centre for Marine Research and Innovation. For each series, five samples were generated, one corresponding to the sea inlet water and four to treated effluents, respectively. A total number of 10 samples (8 from the discharged scrubber water and 2 inlet samples) were collected in 1L amber glass bottles with Teflon septum-caps that were rinsed twice with sampling solution before collecting scrubber water by overfilling the bottle to minimize airspace. The samples were stored at 4 °C until analysis.

2.3. Sample preparation, HRMS analysis and data processing

A previously developed methodology, based on the EPA method 8310, for the determination of GC-amenable pollutants in river water samples was followed for the extraction of the analytes (Panagopoulou, 2019). Details about the method and the quality control and assurance are provided in the supplementary material (Table S1). Samples were analyzed in a GC system (Bruker 450 GC), equipped with an autosampler (CP-8400), coupled to a hybrid QTOF-HRMS (Maxis Impact, Bruker Daltonics). Chromatography separation was performed by gradient and using a Restek Rxi-5Sil MS column with a length of 30 m (0.25 mm i.d. x 0.25 µm film thickness) and in splitless mode, with helium as carrier gas (1.5 mL min⁻¹). The QTOF mass spectrometer was equipped with an APCI ionization source operated in positive ionization mode. HRMS data were acquired in two different approaches: a) Data Independent Acquisition (DIA) in broadband collision-induced dissociation (bbCID) and b) Data Dependent Analysis (DDA) in Auto MS/MS. More details are included in the supplementary material.

For the identification of alkyl-PAHs, a suspect screening approach was used. For that, a data processing workflow was developed using TASQ Client 2.1 and DataAnalysis 5.1 software (Bruker Daltonics, Bremen, Germany). An in-house exact mass database was used for compound identification, including the 16 parent PAHs and a wide range of relevant alkyl-derivatives, covering up to four degrees of alkylation (C1–C4 indicating methyl, ethyl, propyl, isopropyl, butyl, and isobutyl congeners) (Cooper, 2003; Lunde Hermansson et al., 2021). Considering that several isobaric compounds were included in the suspect list, the suspects were grouped based on their molecular formula creating 26 suspect groups for screening purposes, as described in the supplementary material, Table S2.

The criteria followed to identify the tentative candidates in the suspect screening is described in Fig. 1 and were: (i) procedural blank evaluation, and subtraction of the compounds that their intensity area was not, at least, ten times higher than that found in the samples; (ii) an intensity threshold (100–200 counts, equivalent to a signal to noise ratio of ≥ 10), (iii) accurate mass measurements of the molecular ion $[M]^+$ and protonated molecule $[M+H]^+$, with a mass tolerance of ± 2 mDa, (iv) a good isotopic fit, based on molecular formula (≤ 100 mSigma) and (v) when possible, the identification of at least one characteristic fragment ion and their accurate masses. For positive findings, an in-depth evaluation of the fragmentation (MS/MS) spectra, combining both DIA and DDA data, was performed considering only the chromatographic peaks with the highest intensity in cases of suspected isomeric clusters, and these spectra were compared with available databases (e.g. NIST and Mass Bank databases). A score $>70\%$ was set as a threshold to indicate a good matching between the theoretical and experimental spectra. For the suspects that fulfilled these criteria, their chromatographic pattern was evaluated, by comparing the experimental and theoretical cluster profile, obtained from the scientific literature. Furthermore, the plausibility of their chromatographic retention time (RT) was also investigated, taking as a reference the isotopically labelled-PAHs (IS-PAHs). The confidence in the identifications was provided according to the hierarchical degrees of certainty described by Schymanski et al. (2014). According to this approach, level 1 is achieved with the unequivocal identification using analytical standards, while for level 2, unequivocal information on the fragmentation pattern is required to assign a tentative molecular structure. Finally, level 3 is

Workflow for the identification of suspects

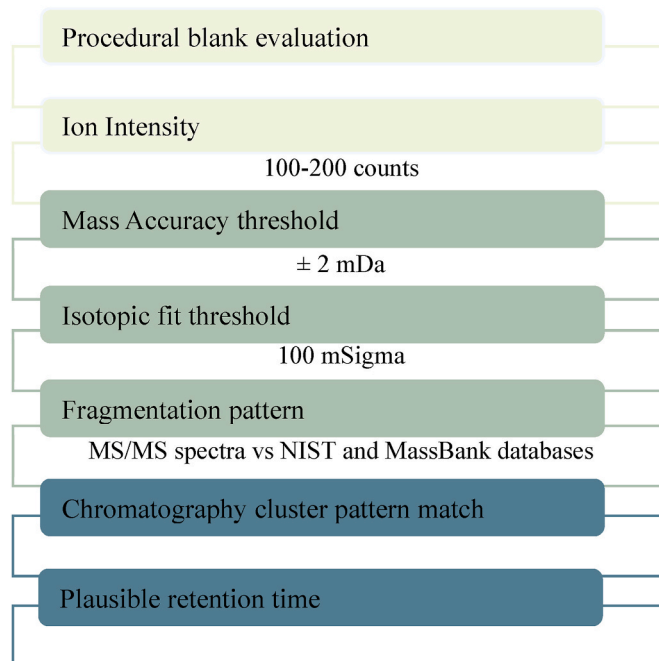


Fig. 1. Data treatment workflow for the identification of suspect compounds.

achieved with information on the fragmentation that suggests a tentative molecular structure.

2.4. GC-MS/MS confirmation of identified alkyl PAHs derivatives

For the final confirmation of the identified suspect hits, samples were re-processed in a GC (Thermo Trace 1300 Series) triple quadrupole instrument (TQS 9000 series). GC separation was carried out on a Thermo Scientific TraceGOLD TG-1701MS (30 m × 0.25 mm × 0.5 µm) using a similar chromatographic gradient as in the GC-APCI-QTOF analysis. Compound identification was done by multiple reaction monitoring (MRM) mode using the transitions optimized by Sørensen et al. (2016a). Further details are included in the supplementary material (Table S3). Analytical standards representative for the different alkyl homologues detected were used. Their selection was based on the approach by Yang et al. (2014a), who evaluated the performance of a wide range of alkylated standards for the quantification of the different homologue clusters.

2.5. Retrospective analysis workflow

A retrospective analysis was carried out to identify other relevant organic contaminants of potential concern in scrubber waters and assess their distribution and occurrence in the samples. For this purpose, a second in-house suspect list was used, including compounds that are widely detected in fuels (Alexander et al., 1986; Trolie et al., 1999; Yang et al., 2014a) and occurring in petroleum contaminated sites, covering various heteroaromatics derivatives, as listed in Table S4 (Carrizo et al., 2015; Han et al., 2019; Park et al., 2018; Walgraeve et al., 2010; Wei et al., 2015). This compound database collects other (poly)cyclic aromatic compounds (PACs) such as benzene, biphenyl and phenol, PACs with a sulphur (benzothiophene, dibenzothiophene and naphthobenzothiophene) and an oxygen element in their structure (benzofuran and dibenzofuran) and, nitro and oxy PAHs derivatives. Samples were processed using the same criteria as described in section 2.3.

3. Results and discussion

3.1. Identification of suspect PAHs and alkyl derivatives

The identification of suspect alkyl-PAHs derivatives by GC-APCI-HRMS is a challenging task, considering (i) the lack of relevant scientific literature and/or reference standards and GC-HRMS spectra databases, (ii) their low fragmentation due to their polycyclic structure, (iii) the presence of several isomeric compounds with similar fragmentation profile and (iv) the non-availability of a RT prediction model for GC-

amenable compounds to support the identification and enable the structure elucidation of isomeric compounds. To enhance compound identification and achieve more structural information, samples were injected in both DIA and DDA mode.

The suspect screening strategy, together with a manual revision of the extracted-ion chromatograms (XIC) and the MS/MS spectra, allowed the identification of 7 parent PAHs and 12 suspect isomeric groups, as listed in Table 1. According to the level-based identification scheme presented by Schymanski et al. (2014), most of the suspects were identified under level 3, due to the lack of analytical standards for full

Table 1

List of identified compounds from combination of suspect (GC-HRMS) and target (GC-MS/MS) strategies.

Suspect group/Compound		Molecular formula	Exact mass (m/z)	Measured mass (m/z)	Ion	Standards of selected Isomers	Identification level by (GC-HRMS)	Identification level by (GC-MS/MS)		
Suspect 1	Naphthalene	C ₁₀ H ₈	128.0621	129.0700	[M+H] ⁺		1			
Suspect 7	Acenaphthene	C ₁₂ H ₁₀	154.0777	155.0859	[M+H] ⁺		1			
Suspect 8	Fluorene	C ₁₃ H ₁₀	166.0777	167.0861	[M+H] ⁺		1			
Suspect 12	Phenanthrene	C ₁₄ H ₁₀	178.0777	179.0874	[M+H] ⁺		1			
Suspect 17	Fluoranthene	C ₁₆ H ₁₀	202.0777	203.0865	[M+H] ⁺		1			
Suspect 19	Pyrene						1			
	Chrysene	C ₁₈ H ₁₂	228.0934	229.1021	[M+H] ⁺		1			
Suspect 2	Naphthalene-C1	C ₁₁ H ₁₀	142.0777	143.0860	[M+H] ⁺	2-methylnaphthalene	2	1		
Suspect 3	Naphthalene-C2	C ₁₂ H ₁₂	156.0934	142.0784	[M] ⁺	1-methylnaphthalene	2	1		
				157.1012	[M+H] ⁺	2-ethylnaphthalene	2	1		
				156.0944	[M] ⁺	1-ethylnaphthalene	2	1		
						2,6-dimehtylnaphthalene	3	1		
Suspect 4	Naphthalene-C3	C ₁₃ H ₁₄	170.1090	171.1168	[M+H] ⁺	Dimethylnaphthalene	3	2		
						2-isopropylnaphthalene	3	1		
						170.1104	[M] ⁺	1,3,7-trimethylnaphthalene	3	1
								2,3,5-trimethylnaphthalene	3	1
Suspect 5	Naphthalene-C4	C ₁₄ H ₁₆	184.1247	185.1332	[M+H] ⁺	Trimethylnaphthalene	3	2		
						1,4,6,7-tetramethylnaphthalene	3	1		
						184.1260	[M] ⁺	1,2,5,6-tetramethylnaphthalene	3	1
								Tetramethylnaphthalene	3	2
Suspect 9	Fluorene-C1	C ₁₄ H ₁₂	180.0934	181.1018	[M+H] ⁺	1-methylfluorene	3	1		
Suspect 10	Fluorene-C2	C ₁₅ H ₁₄	194.1090	180.0947	[M] ⁺	Methylfluorene	3	2		
				195.1179	[M+H] ⁺	1,7-dimethylfluorene	3	1		
Suspect 11	Fluorene-C3	C ₁₆ H ₁₅	208.1247	194.1107	[M] ⁺	Ethyl/Dimethylfluorene	3	2		
				209.1332	[M+H] ⁺	9-n-propylfluorene	3	3		
Suspect 13	Phenanthrene-C1	C ₁₅ H ₁₂	192.0934	208.1262	[M] ⁺	Trimethylfluorene	3	3		
				193.1019	[M+H] ⁺	1-methylphenanthrene	3	1		
Suspect 14	Phenanthrene-C2	C ₁₆ H ₁₄	206.1090	192.0951	[M] ⁺	Methylphenanthrene	3	2		
				207.1177	[M+H] ⁺	3,6-dimethylphenanthrene	3	1		
				206.1107	[M] ⁺	1,3-dimethylphenanthrene	3	1		
						1,2-dimethylphenanthrene	3	1		
Suspect 15	Phenanthrene-C3	C ₁₇ H ₁₆	220.1247	221.1335	[M+H] ⁺	Dimethylphenanthrene	3	2		
						2,6,9-trimethylphenanthrene	3	1		
						220.1265	[M] ⁺	1,2,6-trimethylphenanthrene	3	n.d
								Trimethylphenanthrene	3	2
Suspect 16	Phenanthrene-C4	C ₁₈ H ₁₈	234.1409	235.1487	[M+H] ⁺	1-methyl-7-isopropyl-phenenthrene	3	1		
						234.1425	[M] ⁺	1,2,6,9-tetramethylphenanthrene	3	n.d
								Tetramethylphenanthrene	3	n.d
						Suspect 18	Fluoranthene/ Pyrene-C1	C ₁₇ H ₁₂	216.0934	217.1022
216.0954	[M] ⁺	1-methylpyrene	3	1						
							3	n.d		

confirmation and the non-availability of GC-APCI-HRMS spectra database for direct comparison, except for parent PAHs and few alkyl derivatives where level 1 and 2 could be achieved (Table 1).

For the identification of the parent PAHs, the MS/MS spectra of the positive findings were compared with an open-source library (Mass Bank Europe) with a match score higher than 70. Furthermore, their RT was matched with that of the IS-PAHs. The priority PAHs identified in the samples were acenaphthene, chrysene, fluorene, fluoranthene, naphthalene, phenanthrene and pyrene. These findings match well with the study performed by Lunde and colleagues (Lunde Hermansson et al., 2021) about the occurrence of 16 priority PAHs in open and closed loop scrubber systems, where the low molecular weight PAHs (2–4 rings) were found at higher concentrations than the high molecular compounds. In these samples, naphthalene and phenanthrene were also the dominating substances, in terms of concentration, followed by fluorene and pyrene.

For the alkyl-PAHs, besides exact mass measurements of the precursor ion and the good isotopic fit, the presence of the characteristic fragments was used as evidence for their identification (Table S5). Since the compounds detected covered alkyl homologues with up to four alkyl substituents, the product ions resulting with the loss of H^+ , CH_3^+ , $C_2H_5^+$ and $C_3H_7^+$ were investigated in the samples to support their occurrence. In addition, the ring and double bond equivalents (RDB) was also used to confirm their identification, as aromatic compounds have a high RDB (≥ 7) and it increases with a higher number of benzene rings. Furthermore, the match between the experimental and theoretic chromatographic pattern was used as an additional factor to evidence the identification of the alkyl-PAHs. Fig. 2 shows an example for the identification of naphthalene-C2 compounds using the described protocol. The tentatively identified isomeric groups covered mostly the alkyl derivatives of the parent PAHs present in scrubber water, such as

naphthalene, fluorene, phenanthrene, fluoranthene and pyrene derivatives, as listed in Table 1. However, those corresponding to naphthalene and fluorene were the most frequent, and among these, the methyl (C1) derivatives were the most prominent.

For the alkyl naphthalenes (Fig. 3a), homologues covering from one to four degrees of alkylation were identified (suspect groups 2–5 in Table 1 and S5). Suspect group 2 corresponds to methylnaphthalene (MN) isomers (m/z : 142.0777), 1-MN and 2-MN, eluting at 10.5 and 10.7 min. Based on the literature evidence using similar chromatographic conditions (Skoczńska and de Boer, 2019), the peaks eluting at 10.5 and 10.7 min were attributed to 2-MN and 1-MN, respectively. Since the chromatographic and fragmentation profiles provided good evidence, these compounds were identified under level 2. Suspect groups 3 correspond to dimethyl (DM) and ethylnaphthalene congeners (m/z : 156.0934), and the XIC showed six chromatographic peaks, eluting from 11.4 to 11.8 min, corresponding to the different isomers. Even though these compounds are structurally alike, with common chromatographic properties, some studies could differentiate among the different isomers, being the ethylated analogues the ones eluting first (Sørensen et al., 2016a; Wang and Edwards, 2007). Based on this information, the chromatographic peaks eluting at 11.4 and 11.45 min may be attributed to 2-ethyl and 1-ethylnaphthalene, while the other four may be assigned to the DM-naphthalene isomers. According to the fragmentation and chromatographic information, ethylnaphthalene isomers could be identified under confidence level 2, while the DM-naphthalene homologues were classified under level 3 due to the unavailability of the chromatographic elution pattern for comparison. For suspect group 4 (m/z : 170.1090) and group 5 (m/z : 184.1247) the XIC showed isomeric clusters of a too great complexity to their identification. In both cases, the evaluation of the MS and MS/MS spectra was performed considering only the peaks with the highest intensity to

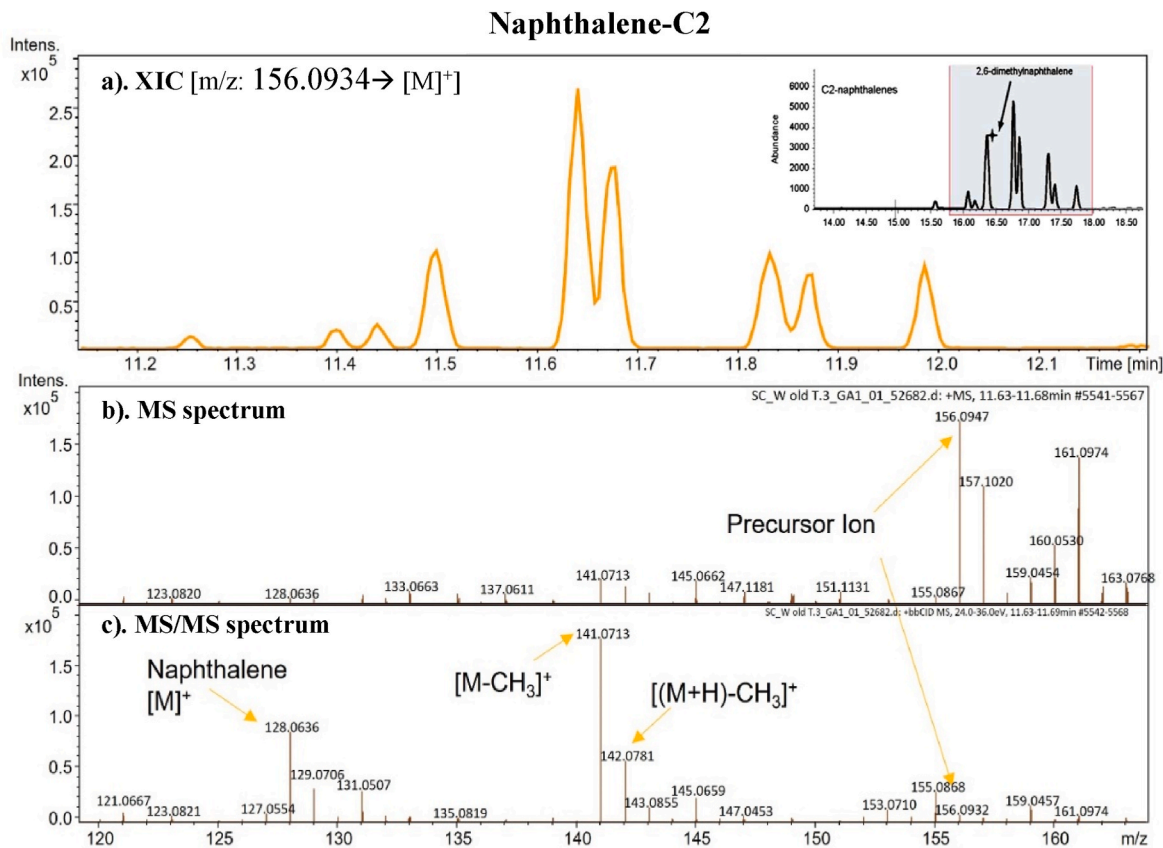


Fig. 2. Example of suspect identification of Naphthalene-C2 compounds. a) Experimental (and theoretical at the top right corner) Extracted Ion chromatogram (XIC), b) experimental full-scan MS spectrum (RT: 11.65 min) and c) experimental MS/MS spectrum (RT: 11.65 min) of suspect compound with m/z 156.0934.

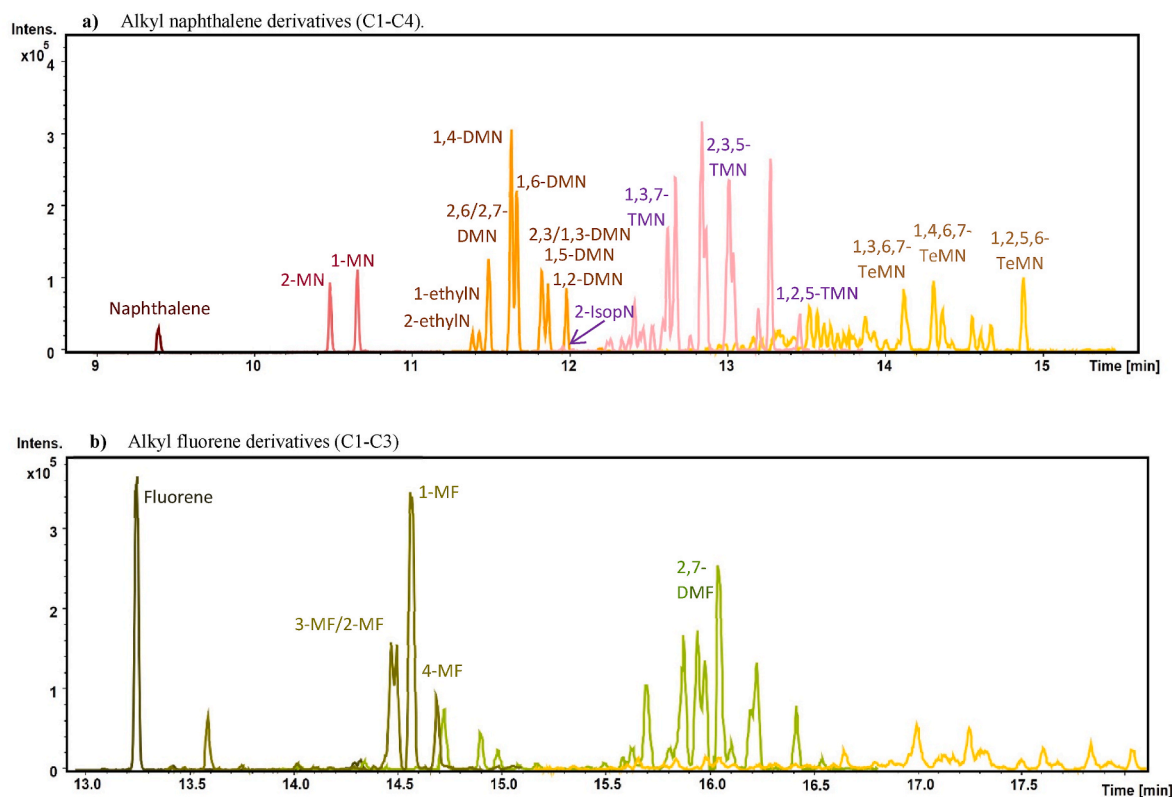


Fig. 3. Extracted ion chromatograms of the tentatively identified alkyl derivatives of a) naphthalene (C1–C4) and b) fluorene (C1–C3). *MN (methylnaphthalene), DM (dimethylnaphthalene), IsopN (isopropylnaphthalene), TMN (trimethylnaphthalene), TeMN (tetramethylnaphthalene), MF (methylfluorene) and DMF (dimethylfluorene).

compare with the reference NIST spectra. In this way, suspect group 4 was identified as the isomeric cluster eluting from 11.9 to 13.6 and suspect group 5 eluting from 12.5 to 15 min. For these clusters, besides the fragmentation information, the comparison of the chromatographic pattern with that observed in the scientific literature in crude oils (Sørensen et al., 2016a; van Aarssen et al., 1999) was crucial for assessing their identification. With this evaluation, it could be observed that trimethyl (TM) and tetramethyl (TeM) isomers were the dominant ones in comparison with the other alkyl substituents. However, due to the complexity in the chromatographic profile and limited fragmentation information, these compounds could be identified under level 3 only.

Regarding alkyl fluorenes (Fig. 3b), which are the suspect groups 9–11 (Table 1 and S5) and that correspond to fluorene C1–C3, all substances were tentatively identified under level 3 of confidence. The XIC shows greater complexity of the isomeric clusters with the increasing degree of alkylation. As in the case for naphthalene derivatives, characteristics fragments were evaluated ($[M - H]^+$, $[M - CH_3]^+$, $[M - C_2H_5]^+$, $[M - C_3H_7]^+$) and the chromatographic pattern was compared with that in the literature, to tentatively identify the presence of these alkyl homologues in the samples (Li et al., 2013; Sørensen et al., 2016a; Yang et al., 2014b). The suspect groups 13–16 (Table 1 and S5) were associated with phenanthrene and anthracene alkyl derivatives, while the group 18 was linked with fluoranthene and pyrene derivatives with only one methyl group (Figure S1b). The positive findings for phenanthrene/anthracene homologues (Figure S1a) included also compounds with one to four degrees of alkylation, being methyl and DM-phenanthrene the dominant isomers. Since these isomeric clusters are more complex than those derived from naphthalene and fluorene, all these compounds were identified under level 3 of confidence (Budzinski et al., 1992; Emsbo-Mattingly and Litman, 2016; Sørensen et al., 2016b; Webster et al., 2009).

A similar profile of target compounds has been detected in studies

aiming to characterize exhaust from different seagoing ships (Cooper, 2001, 2003), and on evaluating the pollution of vulnerable areas due to industrial activities or intense marine traffic (Hong et al., 2016; Wang et al., 2014; Yuan et al., 2015). In these studies, the compounds showing the highest concentrations were naphthalene and phenanthrene as well. However, very few alkyl-PAHs were considered, and when detected, they only included naphthalene C1–C3 and phenanthrene/anthracene-C1.

3.2. Confirmation by GC-MS/MS analysis

To achieve a higher degree of certainty in the identification of the alkyl PAHs derivatives, samples were re-injected in GC-MS/MS instrument. For this, 22 representative standards were selected to determine the presence of the isomeric clusters and to define the RT identification windows. With the MRM analysis (Table S3), the alkyl homologues present in the samples could be identified with high confidence. However, as it was not possible to purchase standards for every single isomer, but just for some representative substances, the certainty in compound identification increased from level 3 to level 2 for most alkyl-PAHs (Table 1). The full confirmation under level 1 could only be reached for few compounds: a) compounds that eluted as individual substances, such as 1 and 2-methylnaphthalene (suspect group 2), and 1 and 2-ethylnaphthalene (suspect group 3) and b) isomers within a cluster that matched with the spiked reference standards, as depicted in Figure S2 and S4, for naphthalene and phenanthrene PAHs derivatives. These figures show a spiked scrubber water extract with the 22 reference standards, and the peaks corresponding to the spiked specific isomers show a clear increase in intensity in the chromatographic profile.

As an example, for naphthalene-C2 (Figure S2a), 2-ethyl, 1-ethyl and 2,6-DM naphthalene was selected to confirm ethyl isomers and to identify the first eluting peak representative for the DM isomer cluster, and the RT window for their identification was defined from 8 to 8.6

min. For this cluster, only one transition, corresponding to the loss of methyl ($[M]^+ \rightarrow [M - CH_3]^+$) was recorded to identify both ethyl and methyl groups. For naphthalene-C3 (Figure S2b), 3 different compounds were selected as reference standards, 2-isopropyl, 1,3,7-TM and 2,3,5-TM naphthalene because they eluted at the beginning, in the middle and at the end of the isomeric cluster, and the defined RT window was from 8.3 to 10 min. For the MRM transitions, to obtain information to identify the whole cluster, two different transitions were monitored that were indicators of the following losses: $[M]^+ \rightarrow [M - CH_3]^+$ (methyl) and $[M]^+ \rightarrow [M - C_2H_5]^+$ (ethyl) (Figure S3a). Thus, with the first transition, representative homologues having ethyl, methyl or isopropyl substituents could be monitored (e.g. TM, ethyl-methyl and isopropyl naphthalene) while the second transition ($[M - C_2H_5]^+$) is representative for n-propyl substituents. For naphthalene-C4, 1,4,6,7-TeM and 1,2,5,6-TeM-naphthalene were selected as reference standards, as they

elute in the middle and at the end of the cluster defining a RT window from 9 to 12 min (Figure S2c). In this case, three transitions are needed to obtain structural information for the full cluster ($[M]^+ \rightarrow [M - CH_3]^+$, $[M]^+ \rightarrow [M - C_2H_5]^+$ and $[M]^+ \rightarrow [M - C_3H_7]^+$) (Figure S3b). With the first one ethyl, methyl and *t*-butyl substituents can be monitored, the second one is indicative for methyl and a propyl groups, while the last one ($[M]^+ \rightarrow [M - C_3H_7]^+$) is representative for isobutyl groups. For the other substances, a similar fragmentation profile is observed, as described in the supplementary material.

3.3. Identification of other relevant PACs by retrospective analysis

After applying the identification criteria described in section 2.3, the initial database was reduced to 18 suspect groups detected in the samples. The exact masses of the tentatively identified compounds,

Table 2
Retrospective analysis results by GC-HRMS.

Suspect group/Compound	Examples of Isomers	Molecular formula	Exact mass (m/z)	Measured mass (m/z)	Ion	Identification Level by (GC-HRMS)
Suspect 9 Biphenyl		C ₁₂ H ₁₀	154.0777	155.0858	$[M+H]^+$	3
Suspect 10 Biphenyl-C1/	Methylbiphenyl	C ₁₃ H ₁₂	168.0934	154.0785 169.1017	$[M]^+$ $[M+H]^+$	3
Suspect 11 Diphenylmethane				168.0946	$[M]^+$	
Biphenyl-C2/	Ethyl/Dimethyl-biphenyl	C ₁₄ H ₁₄	182.1090	183.1175	$[M+H]^+$	3
Suspect 12 Diphenylmethane-C1	Methyldiphenylmethane			182.1104	$[M]^+$	
Biphenyl-C3	Trimethylbiphenyl	C ₁₅ H ₁₆	196.1247	197.1335	$[M+H]^+$	3
Suspect 16 Phenol-C2	Xylenol	C ₈ H ₁₀ O	122.0726	196.1262 123.0809	$[M]^+$ $[M+H]^+$	3
Suspect 17 Phenol-C3	Mesitol	C ₉ H ₁₂ O	136.0883	122.0733 137.0966	$[M]^+$ $[M+H]^+$	3
Suspect 19 Dibenzofuran	Propylphenol	C ₁₂ H ₈ O	168.0570	136.0881 169.0652	$[M]^+$ $[M+H]^+$	3
Suspect 20 Dibenzofuran-C1	Methyldibenzofuran	C ₁₃ H ₁₀ O	182.0726	168.0584 183.0812	$[M]^+$ $[M+H]^+$	3
Suspect 21 Dibenzofuran-C2	Ethyldibenzofuran	C ₁₄ H ₁₂ O	196.0883	182.0740 197.0969	$[M]^+$ $[M+H]^+$	3
Suspect 26 Dibenzothiophene	Dimethyldibenzofuran	C ₁₂ H ₈ S	184.0341	196.0897 185.0432	$[M]^+$ $[M+H]^+$	3
Suspect 27 Dibenzothiophene-C1	Methyldibenzothiophene	C ₁₃ H ₁₀ S	198.0498	184.0362 199.0585	$[M]^+$ $[M+H]^+$	3
Suspect 28 Dibenzothiophene-C2	Ethyldibenzothiophene	C ₁₄ H ₁₂ S	212.0660	198.0517 213.0741	$[M]^+$ $[M+H]^+$	3
Suspect 36 Fluorenone	Dimethyldibenzothiophene			212.0662	$[M]^+$	
	9H-Fluoren-9-one	C ₁₃ H ₈ O	180.0570	181.0661	$[M+H]^+$	3
Suspect 37 Anthranone		C ₁₄ H ₁₀ O	194.0726	180.0584 195.0814	$[M]^+$ $[M+H]^+$	3
Suspect 38 4H-Cyclopenta[def]phenanthren-4-one		C ₁₅ H ₈ O	204.0570	194.0726 205.0659	$[M]^+$ $[M+H]^+$	3
Suspect 39 Benzanthrone		C ₁₇ H ₁₀ O	230.0726	204.0586 231.0817	$[M]^+$ $[M+H]^+$	3
Suspect 45 Benzofluorenone				230.0746	$[M]^+$	
Phenanthrenequinone	1,4-phenanthrenequinone	C ₁₄ H ₈ O ₂	208.0519	209.0609	$[M+H]^+$	3
Suspect 46 Anthraquinone	9,10-anthraquinone			208.0535	$[M]^+$	
Anthraquinone-C1	1,4-anthraquinone			204.0586	$[M]^+$	
	2-methylanthraquinone	C ₁₅ H ₁₀ O ₂	222.0675	223.0769	$[M+H]^+$	3
				222.0695	$[M]^+$	

together with their molecular formulas and possible structures, are presented in Table 2. As it occurs for alkyl-PAHs, several isomers co-elute, having a complex chromatographic and fragmentation profile. Thus, these substances could be identified under level 3 of confidence, and level 1 could not be reached due to the lack of analytical standards. For some of them, it was not possible to achieve enough MS/MS evidence to get level 2. However, other information was used, such as the plausible RT, based on literature, the $RBD > 7$ and the match between the experimental and theoretic chromatography pattern, according to the literature, supporting their tentative identification in the samples. The detected suspect groups include biphenyls, phenols, dibenzothiophenes, dibenzofurans and some of the oxy-PAHs derivatives. For suspect groups with alkylated substituents, the loss of H^+ , CH_3^+ , $C_2H_5^+$ and $C_3H_7^+$ was observed depending on the degree of alkylation. On the other hand, the characteristic loss of CO was observed in all oxygenated PAHs groups, also supporting their occurrence in the samples (Table S6).

For biphenyls, suspect groups from 9 to 12 (Table 2 and S6) both parent and alkyl derivatives were found, eluting from 11.2 to 14.9 min. In the cases of suspect groups 10 (m/z : 168.0934) and 11 (m/z : 182.1090), they could be attributed to diphenylmethanes or biphenyls. However, according to the literature, biphenyls are the major components detected in crude oils (Trolie et al., 1999) so the detection of the exact masses m/z : 168.0934 and m/z : 182.1090 are mostly attributed to biphenyl and their alkyl derivatives. The presence of their characteristic fragments, $RBD > 7$, and a plausible RT (11.2–14.9 min) were taken as evidence for their occurrence. According to Alexander et al. (1986) there is a relationship in the elution time between biphenyl and naphthalene alkyl derivatives (10.5–15 min), thus helping in their identification. In the case of alkyl phenols, suspect groups 16 (phenol-C2, m/z : 122.0726) and 17 (phenol-C3, m/z : 136.0883), the structural information complied suggest their occurrence in the samples. However, the lack of theoretic chromatographic profiles to match with the experimental fingerprint and the unavailability of fragments to compare with MS/MS libraries does not allow for a full confirmation of their identity with a high degree of certainty.

The detected PACs with an oxygen element in their structure were dibenzofuran and some of their alkyl homologues (suspect groups 19–21, Table 2 and S6). The XIC of dibenzofuran (m/z : 168.0570), dibenzofuran-C1 (m/z : 182.0726) and dibenzofuran-C2 (m/z : 196.0883) were evaluated. Other relevant PACs containing a sulphur element were dibenzothiophene (m/z : 184.0341), dibenzothiophene-C1 (m/z : 198.0498) and dibenzothiophene-C2 (m/z : 212.0654). Dibenzothiophenes elution profile (15.2–18.8) is similar to phenanthrene (15.5 min) and its alkyl derivatives (16.8–20.7 min) (Emsbo-Mattingly and Litman, 2016; Sørensen et al., 2016b). For dibenzofurans, their RT was from 12.6 to 16.0 min and some studies have shown that these compounds elute approximately between fluorene (13.3 min) and dibenzothiophene (15.2 min) (Li et al., 2013; Sørensen et al., 2016b), and this profile has been also observed in the analysis of scrubber water samples. Oxygenated PAHs with ketones and quinones substituents were also detected in all samples. The compounds tentatively identified were fluorenone (m/z : 180.0570), anthrone (m/z : 194.0726), some isomers of phenanthrenequinone and anthraquinone (m/z : 208.0519), 4H-Cyclopenta[def]phenanthren-4-one (m/z : 204.0570), 2-methyl-antraquinone (m/z : 222.0675), benzofluorenone and benzanthrone (m/z : 230.0726).

The presence of these compounds in scrubber water is plausible as the dibenzothiophenes and dibenzofurans have been widely detected in petroleum products and their occurrence is explained by different geochemical processes, being phenols and bisphenols their potential precursors (Li et al., 2013). On the other hand, several oxy-PAHs have been identified as transformation products or direct combustion products in a wide variety of environmental matrices (soils, sediments, river and coastal waters and flue gases from different combustion processes) (Bandowe and Wilcke, 2010; Lundstedt et al., 2007; Han et al., 2019; Layshock et al., 2010; Albinet et al., 2007). The main compounds found in the environment were fluorenone, 9,10-anthraquinone and

benzofluorenone and they are also compounds related to direct combustion together with 4H-Cyclopenta[def]phenanthren-4-one and benzanthrone (Ramdahl, 1983).

4. Conclusions

This study shows that GC-HRMS is a powerful tool to identify the most relevant alkyl-PAHs in scrubber water. The use of both DDA and DIA provided a lot of structural information for compound identification. However, due to the complexity of the isomeric clusters and the lack of individual standards, only a tentative identification (mostly under level 3) was achieved. The combination of GC-HRMS and GC-MS/MS allowed to increase the level of confidence in compound identification. On the other hand, the possibility of performing a retrospective analysis allowed to identify the presence of other relevant contaminants that were not included in the initial screening, providing broader information on the chemical composition of the samples. All the detected compounds are present in crude oil and petroleum contaminated sites and, consequently, they could be considered as potential markers of scrubber water contamination. The occurrence of these compounds deserves further attention, especially when assessing the toxicity of scrubber effluents to marine ecosystems.

Author contribution

Elisa Garcia: Conceptualization, method development, Formal analysis, Data curation, Writing – original draft, Writing – review & editing; Georgios Gkotsis: Formal analysis & Data curation; Maria-Christina Nika: Formal analysis & Data curation; Ida-Maja Hassellöv: sampling, Conceptualization; Writing – review & editing; Kent Salo: sampling, Conceptualization; Writing – review & editing; Anna Lunde Hermansson: sampling, Conceptualization; Writing – review & editing; Erik Ytreberg: sampling, Conceptualization; Writing – review & editing; Meritxell Gros: Conceptualization, method development, Data curation, Writing – original draft, Writing – review & editing; Mira Petrović: Funding acquisition, Conceptualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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