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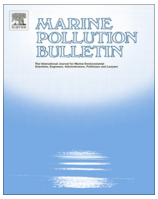

Pyrolysis–gas chromatography–mass spectrometry with electron-ionization or resonance-enhanced-multi-photon-ionization for characterization of polycyclic aromatic hydrocarbons in the Baltic Sea

Stefan Otto [a], Thorsten Streibel [a,b,*], Sabrina Erdmann [a], Sophie Klingbeil [a], Detlef Schulz-Bull [c], Ralf Zimmermann [a,b]

[a] *Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, 18059 Rostock, Germany*
[b] *Joint Mass Spectrometry Centre, Cooperation Group Comprehensive Molecular Analytics, Institute of Ecological Chemistry, Helmholtz Zentrum München-German Research Center of Environmental Health (GmbH), Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany*
[c] *Marine Chemistry, Leibniz Institute for Baltic Sea Research, Seestrasse 15, 18119 Warnemünde, Rostock, Germany*

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH), as a part of dissolved organic matter (DOM), are environmental pollutants of the marine compartment. This study investigates the origin of PAH, which is supposed to derive mainly from anthropogenic activities, and their alteration along the salinity gradient of the Baltic Sea. Pyrolysis in combination with gas chromatography and two mass selective detectors in one measurement cycle are utilized as a tool for an efficient trace analysis of such complex samples, by which it is possible to detect degradation products of high molecular structures. Along the north–south transect of the Baltic Sea a slightly rising trend for PAH is visible. Their concentration profiles correspond to the ship traffic as a known anthropogenic source, underlined by the value of special isomer ratios such as phenanthrene and anthracene (0.31–0.45) or pyrene and fluoranthene (0.44–0.53). The detection of naphthalene and the distribution of its alkylated representatives support this statement.

1. Introduction

Aromatic compounds, especially polycyclic aromatic hydrocarbons (PAH) are widespread pollutants in various compartments of the environment (e.g. Baumard et al., 1999; Broman et al., 1991; Lipiatou et al., 1997; Witt, 1995). They can originate from anthropogenic sources as well as from natural processes (Neff, 1979) and have received increasing scientific interest during the last years (e.g. Motelay-Massei et al., 2006; Pazdro, 2004; Rogowska et al., 2010; Ruczynska et al., 2011; Stader et al., 2013; Witt et al., 2009; Wu et al., 2011). PAH in the marine environment rapidly become associated with particulate matter (Chiou et al., 1998), due to their hydrophobic nature. They are poorly water soluble and in this context their detection by analytical systems is challenging. PAH can be a risk to human health (Ruczynska et al., 2011) and especially the higher molecular-weight aromatics often act carcinogenic and mutagenic (Brody et al., 2007; Shor et al., 2004). Together with their alkylated homologues they show persistence and are nearly resistant to biodegradation (Reunamo et al., 2013). As a general trend it can be observed that smaller PAHs exhibit better biodegradability than larger ones (Thiele-Bruhn and Brummer, 2005). Nevertheless, a high accumulation level of PAH compounds in the sediment (Neff, 1979) results and the global oceans constitutes a large sink for these contaminants (Wang et al., 2007).

PAHs are interacting with dissolved organic matter (DOM) constituents. DOM is defined as organic matter that passes a filter with a pore size near 1 μm including a wide range of constituents (Schwarzenbach et al., 2003). The structural characterization of high molecular PAH as associated DOM constituents, the understanding of its origin and its alteration while being transported to the oceans have hardly been researched yet. PAH can be formed and introduced into the marine environment by various processes, mostly caused by anthropogenic effects, as by-products of chemical processes such as incomplete combustion and pyrolysis of fossil fuel as well as the release into the environment by petroleum spilling or from ships (Pazdro, 2004; Witt, 1995). Natural processes such as oil seeps, plant debris and forest fires have an influence,

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* Corresponding author at: Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, 18059 Rostock, Germany.
E-mail address: thorsten.streibel@uni-rostock.de (T. Streibel).

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too (Wu et al., 2011). In general, a distinction between pyrolytic, diagenetic and petrogenic origin is possible (Lubecki and Kowalewska, 2012).

It is difficult to distinguish between the different PAH sources. The molecular ratios of such compounds as anthracene (ANT) and phenanthrene (PHE) as well as fluoranthene (FLU) and pyrene (PYR) with mass-to-charge-ratios (m/z) of 178 or 202, can provide useful information of the origin of PAH and have the best potential to distinguish between combustion and petroleum sources. For m/z 178, an ANT to ANT plus PHE ratio <0.10 usually is taken as an indicator for petroleum and a higher ratio than 0.10 indicates combustion processes (Yunker et al., 2002). Because of its thermodynamic stability petroleum often contains more PHE than ANT. With the FLU/(FLU + PYR)-value a source evaluation between petroleum, fossil fuel combustion or wood and coal combustion is feasible (Tam et al., 2001; Yunker et al., 2002). On the other hand naphthalene (NAP) is a reliable tracer for contamination by petroleum (Sporstol et al., 1983). In addition, alkyl homologue series of PAH with a maximum at C_1 (monoalkylated) or substances with a higher degree of alkylation are indicator compounds for petroleum, too (Yunker et al., 2002).

The Baltic Sea is an ideal research object, covering a salinity gradient from 2 in the northern area to 25–32 in the southwest (Miltner and Emeis, 2001). Moreover, a large freshwater surplus, mainly from Scandinavian rivers, an only moderate water discharge via North Sea (removal processes) as well as industrial hotspots strongly influence the distribution of PAH compounds. Due to the high residence time (Opsahl and Benner, 1997) its concentration is often 2–10 times higher than the concentration in the North Sea (Witt, 1995). In addition their semi-closed nature surrounded by well developed countries (variety of industry, modern agriculture and high traffic shipping areas) leads to a high environmental load (HELCOM, 2010a; Ruczynska et al., 2011). Riverine runoff and atmospheric input are the two most important vectors of transportation into the marine environments (Lipiatou et al., 1997; Motelay-Massei et al., 2006), whereby the highest concentrations are observed in coastal areas. In addition, a seasonal variation is known, with lowest PAH concentrations in summer and higher concentrations in late autumn (Witt, 1995).

It requires a high degree of resolution power and selectivity to analyze DOM, especially to detect the low concentrated PAH. A variety of analytical systems and methods are available for PAH characterization in water. Often chromatographic techniques such as high performance liquid chromatography (HPLC) in combination with fluorescence detection are used (Ruczynska et al., 2011; Witt, 1995). Gas chromatography (GC) in combination with mass spectrometry (MS) is widespread (e.g. Broman et al., 1991; Baumard et al., 1999). Only sample preconcentration and injection methods such as solid phase extraction (e.g. Witt et al., 2009; Wu et al., 2011) or soxhlet-extraction (Wang et al., 2007) do vary. For a further increase in selectivity and sensitivity for specific tracer molecules in complex samples LASER based methods in MS are indispensable (Li et al., 2010; Stader et al., 2013).

In this study, a chromatographic analysis followed by two different types of mass spectrometers, an electron ionization quadrupole MS (EI-QMS) and resonance-enhanced-multi-photon-ionization time-of-flight MS (REMPI-ToFMS) in combination with the pyrolysis technique was applied to characterize associated PAHs in DOM for the first time in this context. EI is a hard and universal method, by which the identification of compounds is possible through specific fragmentation patterns of the organic molecules, unfortunately it often results in a loss of molecular information. The lack of the molecular ion signal can be prevented by soft ionization techniques such as photo ionization (PI). One such PI technique is Resonance-Enhanced-Multi-Photon-Ionization (REMPI). Especially in combination with GC there are promising developments in terms of selectivity and sensitivity for aromatic hydrocarbons (Fendt et al., 2012; Haefliger and Zenobi, 1998; Imasaka, 2013; Li et al., 2010, 2011; Zimmermann et al., 1995). REMPI selectivity depends on the used photon wavelength as well as on the ionization energy threshold, since the molecules absorb two photons via an intermediate state (Boesl et al., 1981; Boesl, 1991; Mitschke et al., 2006; Zimmermann et al., 1994).

Under pyrolysis conditions high weight molecular species are indirectly accessible as fragments (e.g. regarding heavy crude oil components), which have rarely been analyzed yet. In combination with GC and two mass selective detectors in one measurement cycle, an universal (EI) as well as an aromatic fingerprint (REMPI) result. This system was already successfully applied by Otto et al. (2015a) for crude oil samples. Semi-quantitative compositional changes along the Baltic Sea transect from the north to the southwest by using NAP, FLO, PHE and PYR are described in the literature (Broman et al., 1991). An assignment to anthropogenic sources is possible. In addition, the here used extraction method (Dittmar et al., 2008) was tested for suitability to retain PAH components.

2. Material and methods

This study presents data on the occurrence and distribution of PAH in surface water samples from river Kalix (located in North Sweden) and the Baltic Sea. The river water was sampled during the spring flood in May 2011 (see Herlemann et al. (2014) for detailed information). Marine samples were taken from the Skagerrak (S1) to Bothnian Bay (At4) along salinity gradient (Fig. 1a), while a cruise with the research vessel Meteor (M87/3a) in May and June 2012. The sampling sites and collection methods are described in detail in Otto et al. (submitted for publication) and therefore only a brief description is presented here. Specific sampling dates, depths, salinities and temperatures are listed in Fig. 1b.

2.1. Sample preparation and extraction

Each water sample was collected into a 1 l pre-cleaned glass bottle and separated into dissolved and particulate phase (using 400 °C for 6 h burned glass filters; Whatman, GF/F, diameter 47.0 mm, retention 0.7 µm). The filtered water did undergo a solid phase extraction (SPE) according to the protocol of Dittmar et al. (2008). The cartridges (reverse phase polymeric bond elute PPL cartridges; Agilent) were first conditioned with methanol followed by Milli-Q water acidified with HCl (37 %, Carl ROTH, Karlsruhe) to a pH of 2. One liter Baltic Sea water was extracted with a flow rate of $\sim$30 mL min^{-1} by using a vacuum pump. Afterwards the cartridges were washed with 12 mL Milli-Q water (ph = 2) to remove salt residues. Immediately the adsorber material was dried under pure nitrogen and extracted with 6 mL methanol (ultra LC-MS, Carl ROTH, Karlsruhe). Afterwards the methanolic extract was stored at −20 °C. All glassware used was acid-washed (0.1 M HCl) and dried immediately at 350 °C (except the Schott bottles) for 6 h.

2.2. Measurement system and sample injection

For the analysis, 2 mL of the methanolic extract were preconcentrated to approximately 60 µL under a stream of pure nitrogen. 10 µL were introduced via a quartz vessel in the pyrolysator system (Frontier Laboratories, Douple-Shot-Pyrolyzer, model: PY-2020iD), resulting in about 1 mg of organic material. The pyrolyzer is mounted on a gas chromatograph (HP 5890 Series II), which was coupled to two mass spectrometers for simultaneous application of hard and soft ionization techniques.

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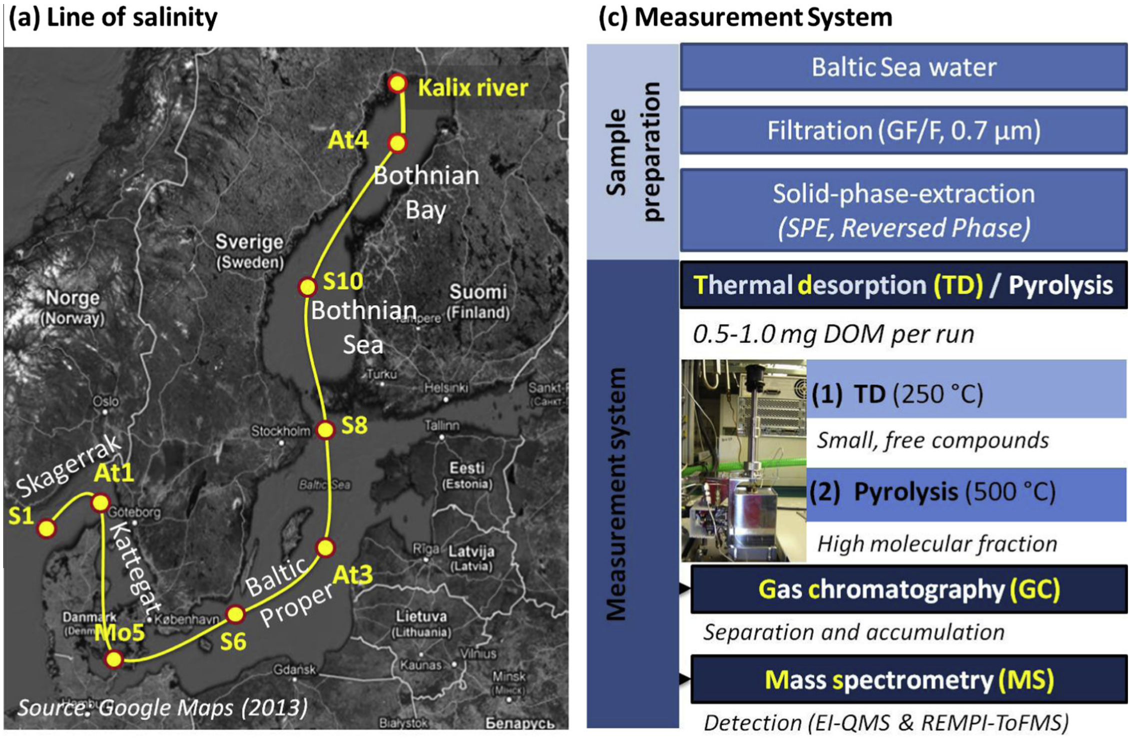

(b) Details for the salinity gradient

Station	Date of sampling	GPS-position		Depth [m]	Temperature [°C]	Salinity [PSU]
S1	2012-05-30	57 00.0995N	006 55.1060E	2.85	11.61	32.06
At1	2012-06-01	58 07.9991N	010 00.0005E	1.70	12.16	30.38
Mo5	2012-05-31	54 42.0068N	010 56.0121E	1.59	12.88	11.68
S6	2012-06-01	55 33.9834N	016 22.0539E	2.70	9.83	7.47
At3	2012-06-02	57 18.3467N	020 04.6968E	3.75	9.07	7.19
S8	2012-06-04	59 21.4864N	020 06.0728E	1.35	6.93	6.31
S10	2012-06-06	61 46.9808N	19 17.6021E	2.33	5.77	5.47
At4	2012-06-05	65 26.7066N	023 17.9074E	1.79	4.32	2.66

Fig. 1. (a) "Meteor" cruise route in summer 2012, with stations of sampling in the Baltic Sea. (b) Location sites in detail. (c) Overview diagram for sample preparation and measurement system.

For the conditioning of the system and the evaporation of the solvent, the sample was flushed with helium in the cooling zone of the pyrolyzer. Helium was also used as carrier gas, with a head pressure of 1 bar. At first the pyrolyzer oven heated up to 250 °C and the sample was pushed into the heating zone for one minute (desorption time). Immediately, a GC/MS measurement followed. Then, the same sample was introduced for a second time, after the oven heated up to 500 °C (pyrolysis step) and the GC/MS cycle started again.

The vaporized chemical compounds in the respective TD and pyrolysis step are separated by the coupled GC system (split mode 1:10; 30 m × 0.25 mm × 0.25 µm non-polar column, SGE-BPX-5). The column temperature was programmed for 60 °C (held for two minute) to 320 °C (held for 12 min) at a rate of 10 °C/min. After the separation process the gas flow was split by a deactivated press fit 3-way Y-Splitter for FS tubing (0.20 –0.75 mm OD) and transferred simultaneously to both connected mass spectrometers. One MS system ionizes via EI, where mass fragments are generated in the positive EI mode with an electron voltage of 70 eV, followed by a quadrupole for separation. The total ion chromatograms (TIC) of EI-QMS are used to characterize compounds with the help of different MS tools (NIST spectral library). If the data base information was inaccurate, standard substances NAP, PHE, PYR (Aldrich Chemistry) and FLO (Acro Organics) were chromatographed. Approximately 100 mg L^{-1} substance were solved in a 1:1 mixture of dichloromethane and *n*-hexane (described in Otto et al., 2015a). For an aromatic fingerprint and an additional proof of relevant PAH compounds a [1+1]-REMPI-ToFMS system was used (Boesl et al., 1981; Boesl, 1991; Zimmermann et al., 1994). For generating REMPI, a Nd:YAG laser (BIG SKY ULTRA, Quantel, Les Uli Cedex, France) with two frequency doubling units yielding 266 nm photons was employed, which corresponds to a photon energy of 4.11 eV. The laser is operated with 10 ns pulse width and a 20 Hz repetition rate exhibiting a power density of approximately 7×10^6 W cm^{-2}. A reflectron ToF-MS (Reflectron CTF10, Kaesdorf Geräte für Forschung and Industrie, Munich, Germany) is utilized for the detection of the molecular ions. More specific device parameters for the REMPI equipment are given in Fendt et al. (2012).

The split ratio after the chromatographic separation at the Y-splitter was 1:100 in favor of the EI-QMS. For calibration and optimization of the REMPI-ToFMS setup a gas standard (Linde

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AG, Pullach, Germany) containing 1 ppm benzene, 1,2,4-trimethylbenzene, benzaldehyde and toluene in nitrogen was used.

3. Results and discussion

The high complexity of DOM is illustrated in Fig. 2 for the northernmost station At4. It allows a first overview through comparison between EI-QMS and REMPI-ToFMS (above and below) as well as TD and pyrolysis (left and right). The abscissa displays the retention time of the GC. Along the ordinate the *m*/*z* value is plotted. The respective intensity of the mass signal is depicted as color bar. The EI-substance spectrum is very complex and superimposed under TD and pyrolysis conditions. The compounds are detected in a mass range between *m*/*z* 40 and 270 for TD. In the pyrolysis step the substance spectrum is expanded and higher signal intensities are visible, with an *m*/*z*-value of approximately 60 up to 320. The ion traces *m*/*z* 73, 207 and 281 become more relevant as a permanent signal at higher GC temperatures (above 250 °C), because these represent siloxane fragments, originating from the column coating. Despite the high complexity of the sample, the EI data can provide reliable information about the structural composition. Furthermore, with regard to aromatic compounds and their alkylated representatives the REMPI-ToFMS data do assist, because the fragmentation is suppressed. It shows an aromatic fingerprint of the sample. A small range of substances is detected with high sensitivity and less complex chromatograms result. If one looks at the measurements under TD conditions in a time window of approximately 400 and 1200 s, with EI a cloud of non-delimitable signals is observed and with REMPI clear signals result. Generally in REMPI, under TD conditions, an aromatic substance spectrum is revealed in a mass range between *m*/*z* 90 and 270. In the pyrolysis step a broader substance spectrum with higher signal intensities between *m*/*z* 60 and 330 is depicted. The aromatic substance spectrum increases significantly toward larger *m*/*z*-values, reflecting a growing number of alkylated species. Taking the At3 (central Baltic Sea) and At1 station (Skagerrak) into consideration (see supplemental material S1), a decrease in signal intensity under TD condition is obvious. Under pyrolysis condition no significant changes are visible.

In the following the semi-quantitative changes of PAH as function of industrial pollution hotspots, (HELCOM, 2014) roughly corresponding with the salinity gradient, is discussed on the basis of selected species: NAP [*m*/*z* 128], FLO [*m*/*z* 166], PHE [*m*/*z* 178] and PYR [*m*/*z* 202]. They were identified by standards and their GC profile is illustrated in Fig. 3a under pyrolysis conditions for the At4 station. These are the most dominant PAH compounds in previous studies (Tam et al., 2001).

Generally, under TD conditions the detectable concentration decreases considerably with increasing salinity due to the dilution of North Sea inflow. In this context the low concentrations of dissolved PAH are challenging. In the pyrolysis step sufficient concentrations for every relevant PAH species are obtained to represent semi-quantitative statements along the Baltic Sea transect from the north to the southwestern station S1. The pyrolysis results are providing adequate peak intensities for all stations.

In different regions of the Baltic Sea different levels of contamination exist. The distribution of PAH is described by Broman et al. (1991). Some stations are almost analogous to the sampling sites described here (SB ~ S6, SA ~ S8, BS ~ S10, BB ~ At4). However, in this study the area of the Skagerrak and Kattegat, which is often neglected, was also taken into consideration. Near the North Sea inflow the salinity change in the surface water of the stations S1 (32 PSU) to Mo5 (12 PSU) and the freshwater inflow is extreme. It will likely have a strong influence on the DOM composition

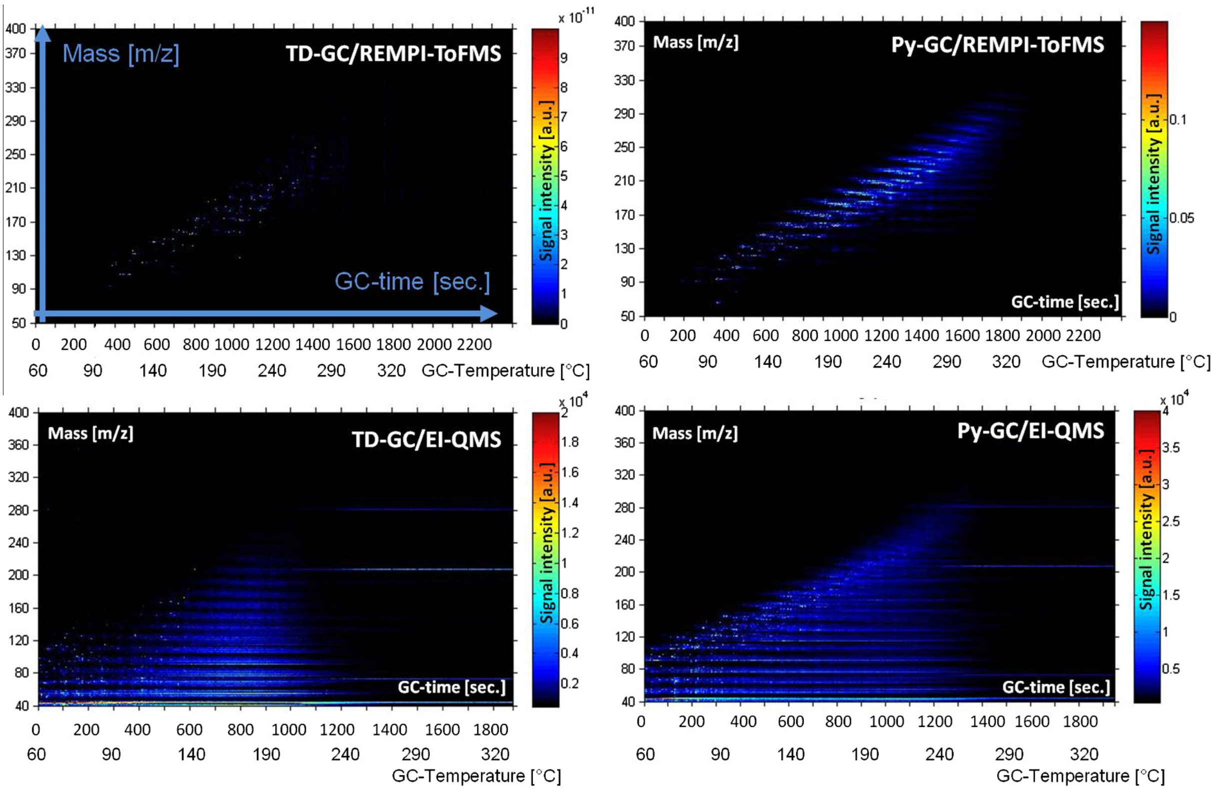

Fig. 2. Direct comparison of the chromatograms resulting from the REMPI-ToFMS (above) and EI-QMS (below) detection for At4 station (Bothnian Bay). The TD step is shown on the left and the pyrolysis step on the right. On the ordinate the GC-time and -temperature is plotted. On the abscissa the mass-to-charge ratio is depicted. Graduated in color are the intensities. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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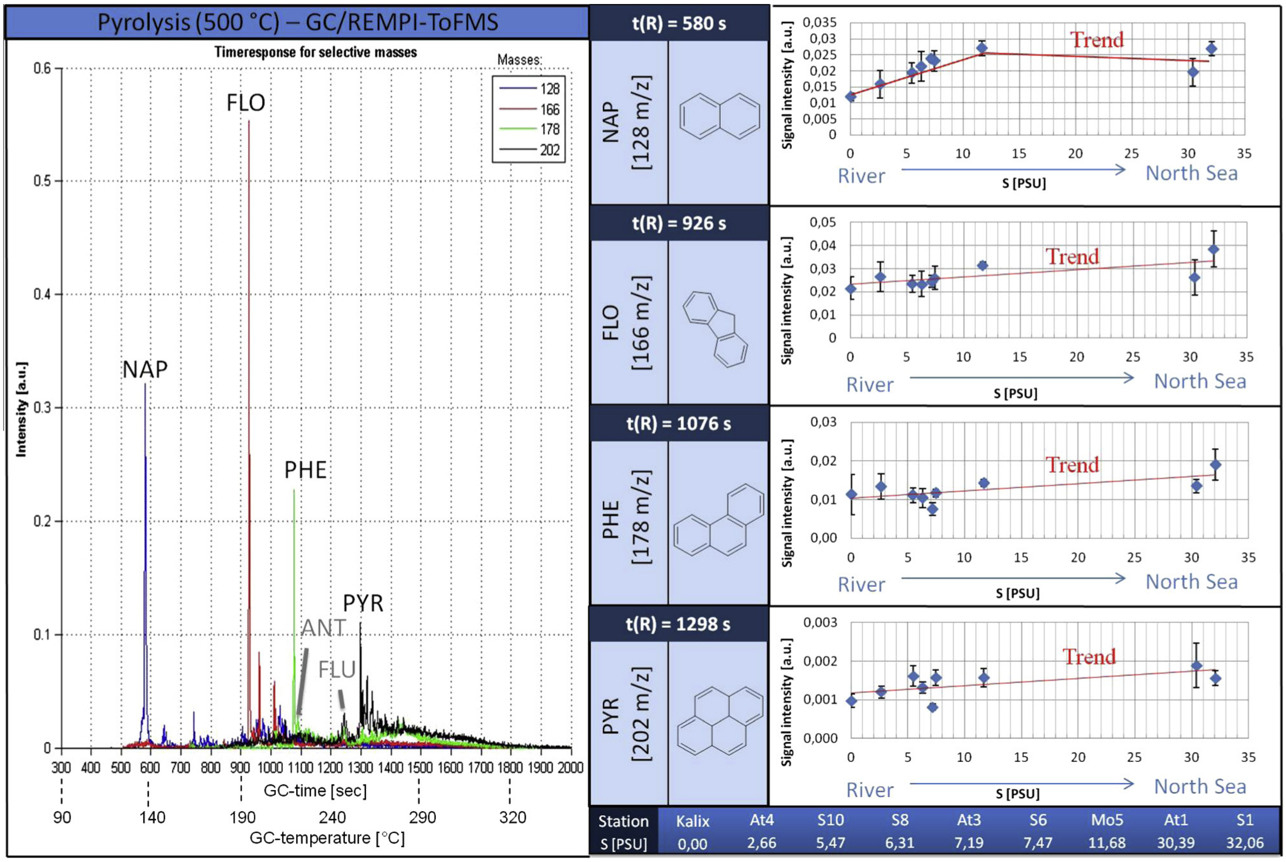

Fig. 3. (a) Chromatogram of At4 surface water samples under pyrolysis conditions, for the ion traces 128, 166, 178 and 202, resulting from the use of REMPI-ToFMS detection. In addition to NAP, FLO, PHE and PYR the time position of ANT and FLU is located in the REMPI-Chromatogram. (b) In the diagrams for the line of salinity the relative peak intensities are given vs. the salinity S. The latter of the respective stations is noted below.

and distribution, as it is well known for the sum parameter of DOM (Sholkovitz, 1976). The impact on the PAH composition is difficult to predict. The aqueous solubility of PAHs has been found to be dependent in most cases on the concentration and type of salt present in solution (Ni and Yalkowsky, 2003). Moreover the Baltic Sea is characterized by high ship traffic, which represents an anthropogenic source for PAH (HELCOM, 2010b).

For data analysis and to obtain particular semi-quantitative results, the peak intensities from the REMPI-chromatograms of the individual molecule ions are used for all stations from the river Kalix (lowest salinity) to the S1 station (highest salinity). Three technical replicates per station for each surface water sample were measured. The relative peak intensities were calculated and are illustrated in Fig. 3b. Therefore, the peak intensity of the REMPI chromatogram for the molecular ion was divided by the total intensities for all nominal masses (90–450 m/z) in a certain time window including the retention time. For NAP (m/z 128, $t(R) = 580$ s) an increasing trend from the river mouth to the Mo5 station (southernmost point of sampling) is observed. After passing Mo5 to S1 station the trend is nearly constant. In general for FLO, PHE and PYR a stagnating to slightly rising trend along the salinity gradient, from the river inflow up to the North Sea is visible. This may be linked to increasing industrial pollution coming along with the gradient of salinity. Although considering pyrolysis fragments of higher aromatic structures in this work, the results show a good agreement to the publication of Broman et al. (1991), where the total concentrations of 11 unbonded PAH was summarized.

Under the assumption that the North Sea input constitutes no relevant source for the PAH components, a slight increase of the PAH content is visible. In the northern Baltic Sea the input of terrestrial organic material by rivers is high (Humborg et al., 2004; Otto et al., submitted for publication), but the industrial development and shipping are low (HELCOM, 2014), explaining the low PAH content. In contrast, in the Baltic Proper and the North Sea channel, higher PAH concentrations are registered. The reason may be the increased ship traffic (HELCOM, 2010b), the higher number of industrialized cities as well as the rivers, partly contaminated by industrial waste, which drain into the southern Baltic Sea.

Linking main sources of PAH in different compartments (northern, central and south-western Baltic Sea) of the marine environment to natural processes and human activities is difficult. The anthropogenic PAH are classified as pyrolytic and petrogenic PAH (Wu et al., 2011). According to Tam et al. (2001) and Yunker et al. (2002) isomer ratios have a good potential to distinguish between natural and anthropogenic sources as well as pyrolytic and petrogenic anthropogenic sources. In this context the ANT/(ANT + PHE)-value and FLU/(FLU + PYR)-ratio were applied. The retention sequence was characterized by measurements of standard solutions. Additionally, the PAH retention indices of Lee (1979) support the evaluation for these substances. There are some selectivity rules that are exploited for peak assignment. The relative cross sections (σ_{rel}) of ANT ($\sigma_{rel} = 3.3$) in comparison to toluene at the utilized wavelength of 266 nm is two orders of magnitude lower than for PHE ($\sigma_{rel} = 178.9$) displayed in Fig. 3a. The same applies to the ratio between FLU ($\sigma_{rel} = 5.8$) and PYR ($\sigma_{rel} = 196.2$) (Otto et al., 2015a). The resulting differences in ionization, in particular of ANT and FLU, are the reason why the EI chromatograms under pyrolysis conditions are used to calculate the isomer ratios. The formation and isomerisation of PAH, if they are released from

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higher molecular structures or build up from smaller, chemically active components (e.g. radicals) under the selected reaction conditions (low pyrolysis temperature, exclusion of air, low pressure) is not probable and can be entirely excluded (Faix et al., 1990). The results for heavy crude oils support the statement, because under pyrolysis conditions next to PHE no peak for ANT was visible (Otto et al., 2015a).

In Kalix river and for At4 (northern Baltic Sea, Bothnian Bay) results an ANT/(ANT + PHE) value between 0.45 and 0.41 and for FLU/(FLU + PYR) a ratio of approximately 0.45 is visible. In the central Baltic (S8, At3) the values are constant by 0.41 or 0.44. Near the North Sea (Mo5, At1, S1) a slight decreasing trend to a value of 0.31 for ANT/(ANT + PHE) was achieved. This corresponds to Yunker et al. (2002) and Tam et al. (2001) suggesting pyrolytic sources over the whole salt gradient. In contrast the FLU/(FLU + PYR) value is nearly constant with a slightly increasing trend toward the North Sea. The range for the line of salinity is 0.4–0.5 and indicating incomplete fossil fuel combustion (Wu et al., 2011). The isomer ratios along the salinity gradient are presented in Fig. 4.

Alkylated PAH can also be used as indicator for an anthropogenic source (Wang et al., 2007). Especially, NAP and its homologues derive mainly from petrogenic inputs (Tam et al., 2001) and constitute a significant fraction of crude oils and petroleum products (Mullins et al., 2007; Otto et al., 2015a). Fig. 5 shows representatives of the NAP homologue row up to the fourth degree of alkylation under pyrolysis conditions. The REMPI-ToFMS chromatograms (right) are compared with the EI-QMS chromatograms (left) for relevant ion traces. On the abscissa the GC-time (-temperature) is plotted and on the y-axis the peak intensity is shown. In the EI chromatogram many peaks can be found on the ion track *m*/*z* 128. Lots of them were only detected by the EI setup and can originate from compound fragmentation of e.g. alkanes. An assignment is often not possible despite database matching due to the complexity of signals, which complicates the identification of components. In contrast the REMPI chromatogram for *m*/*z* 128 is less complex. The dominant NAP peak is visible with a retention time of 580 s. The intensity of ion traces from the first and the second degree of alkylation are increased in both chromatograms. Afterwards for the third and fourth degree of alkylation the intensities decrease significantly, while the product variety is increasing continuously. Similar results are observed for the larger PAH FLO, PHE and PYR.

Using the REMPI setup, high peak intensities for PAH are detected for alkylated species up to the sixth degree auf alkylation (Otto et al., 2015a). NAP and its alkylated representatives were found in the chromatograms resulting from the TD step (supplemental material S2), but with low signal intensities. The free evaporable PAH are barely present. Hence, the investigated organic material mainly consists of large molecular aromatic structures. Alkylated homologues of PAH with maxima at C$_1$ and higher usually indicate mature organic matter or petroleum. For diesel and oil combustion the maxima shift to C$_1$ and higher alkylation degrees (Yunker et al., 2002). For general combustion processes the maximum is mainly located at C$_0$ (Sporstol et al., 1983). In combination with the previously calculated isomer ratios (ANT/PHE and FLU/PYR) a pyrolytic source by incomplete combustion of fossil fuel over the whole salt gradient is probable. This trend is increasing toward the southern and western Baltic Sea, which is in good agreement with the industrial development (HELCOM, 2014) and the more and more densifying shipping routes toward the North Sea (HELCOM, 2010b). The combustion and pyrolytic products of fuels, released into the atmosphere (Pazdro, 2004), are probably the dominant input for PAH to the aquatic environment (Motelay-Massei et al., 2006).

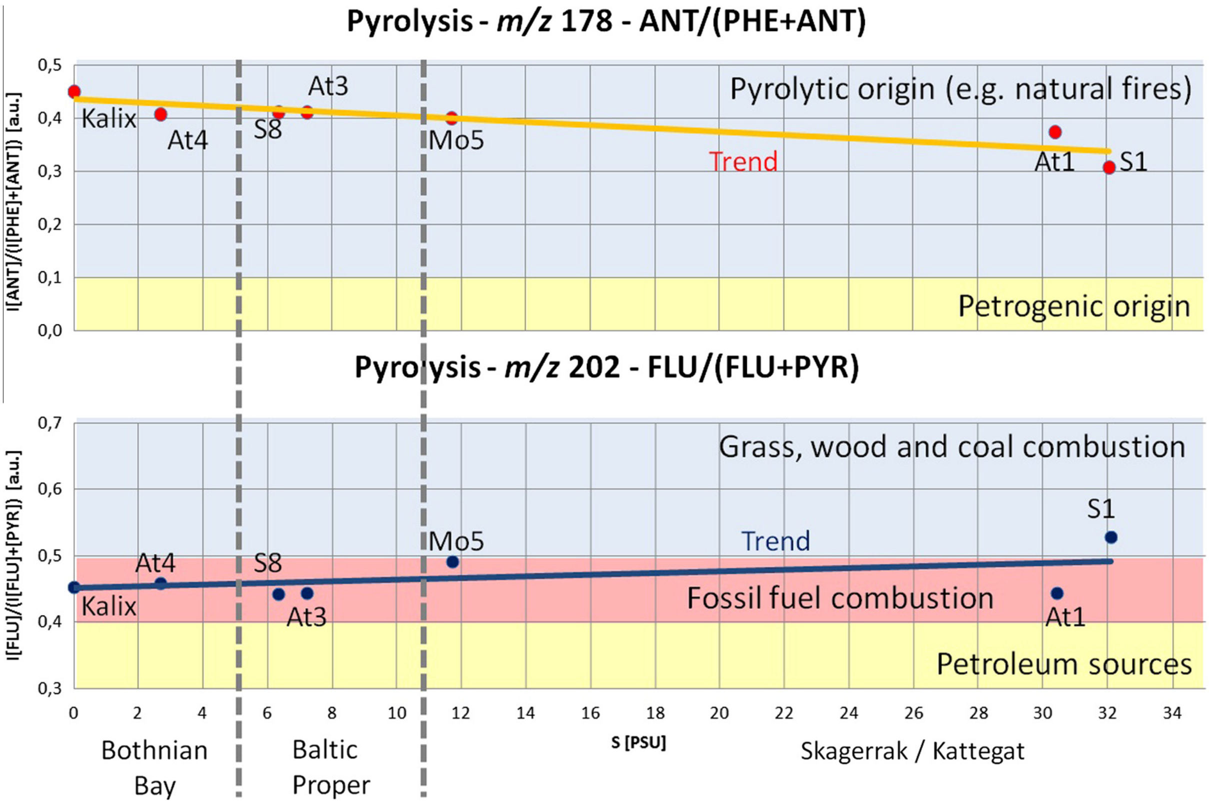

Fig. 4. The isomer ratios ANT/(PHE + ANT) and FLU/(PYR + FLU) are given (ordinate) along the transect (abscissa) of the Baltic Sea under pyrolysis conditions. Each colored area marks a specific source origin. This corresponds with the literature (Yunker et al., 2002; Tam et al., 2001). The trend curve is displayed for semi qualitative statement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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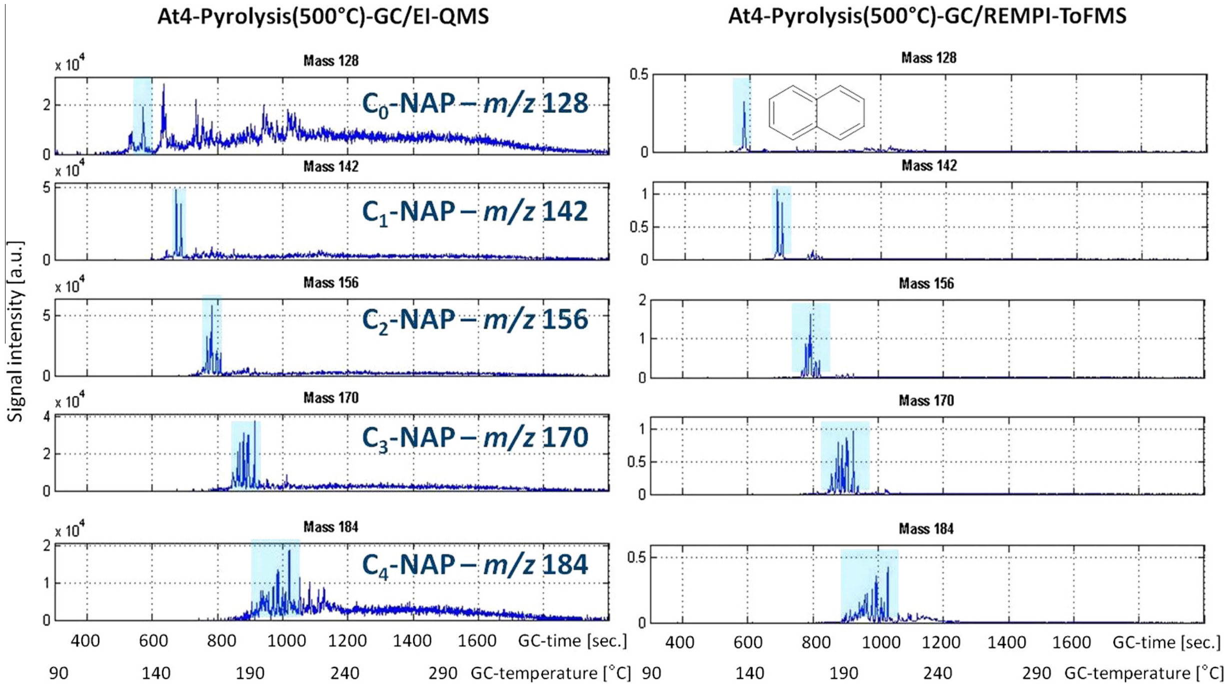

Fig. 5. NAP and its alkylated representatives (C_X) up to the fourth degree of alkylation on the At4 station (Bothnian Bay). Direct comparison of the ion traces which result from EI-QMS (left) and REMPI-ToFMS (right) measurements under pyrolysis conditions. On the abscissa GC-time (parallel the GC temperature) and on the ordinate the peak intensity are plotted.

4. Conclusion

The described Py-GC/MS method with two simultaneous measuring detection units allows an innovative chemical analysis of DOM, which was applied for the first time to investigate PAH compounds in aquatic environments. In addition to the TD step for analysis of the well-studied small PAH components (e.g. Baumard et al., 1999; Broman et al., 1991; Witt, 1995; Witt et al., 2009), a pyrolysis step is necessary to enable the detection of higher molecular degradation products. This field of research is largely unexplored and this study offers an opportunity to gain a first look at the topic.

Referring to the semi-quantitative measurements, a stagnating or slightly rising trend for selected PAH components along the Baltic Sea transect from the north to the southwestern area was visible. Corresponding to the concentration profiles of NAP, FLO, PHE and PYR, their distribution is contrary to the previously investigated lignin degradation products (Otto et al., submitted for publication). This could indicate an anthropogenic input by increasing shipping traffic. That is underlined by the ANT/(PHE + ANT)-value (0.31–0.45) as well as the FLU/(PYR + FLU)-value (0.44–0.53), which is indicative for a release of fossil fuels to the environment by incomplete combustion or pyrolytic processes. The detection of naphthalene and the distribution of its alkylated representatives also support this statement.

The riverine runoff and particularly the atmosphere are the two most important vectors of PAH transportation into the marine systems (Lipiatou et al., 1997; Motelay-Massei et al., 2006). To support this statement, future research should deal with the investigation of all marine environmental compartments of sediment, water and air. For one station in the Baltic Sea the sediment, water column and aerosol should be sampled at the same time. A direct comparison could help to understand exchange processes in more detail. In addition to DOM also the particulate matter should be investigated, because PAH do rapidly adsorb on particles (Neff, 1979). All these types of samples could be measured without time consuming sample preparation by the presented TD/Py-GC-EI-QMS/REMPI-ToFMS system. The separation and a combination of an universal as well as a PAH selective and sensitive detection are useful for a closer look at the high molecular composition of natural samples.

The system could be optimized further by the application of GCxGC systems for a higher separation power (Eschner et al., 2010; Welthagen et al., 2007). Using other wavelengths or increasing LASER repetition frequency (Haefliger and Zenobi, 1998; Li et al., 2011) could expand the substance spectrum and other compounds should be accessible. In summary, the obtained information such as size of aromatic structures, especially under pyrolysis conditions, provides a new access to the research topic of DOM.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2015.08.001.

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