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Assessment of azaarenes and azaarones (oxidized azaarene derivatives) in the Dutch coastal zone of the North Sea

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A B S T R A C T

Azaarenes (oxidized derivatives of azaarenes) is a group of newly emerging chemical compounds. Little is
known about their occurrence in the aquatic environment. Azaarenes are polycyclic aromatic heterocyclic
compounds containing one nitrogen atom in one of the aromatic rings. The (photo) oxidized metabolites of
the azaarenes are often more toxic than the parent compound.

For the first time the concentration of seven azaarenes and seven primary metabolites have been mea-
sured in the surface sediments (fraction < 63 \(\mu\)m) of the Dutch coastal zone of the North Sea. Samples col-
clected in 2000 and 2001 were analyzed using a newly developed method to determine the contents of
azaarenes and azaarones simultaneously in a single GC–MS run.

The concentrations of acridine, benz[a]acridine, benz[c]acridine and 5,6-benzoquinoline varied
between 10–63, 3.9–25, 3.3–11 and 3.98–10.84 ng g\(^{-1}\), respectively. Concentrations of 7,8-benzoquinino-
line and phenanthridine were below the limit of detection. 2-Hydroxyquinoline and 5-hydroxyquinoline,
were present in relatively high concentrations: 7.4–949 and 11–188 ng g\(^{-1}\).

A gradient was observed with highest concentrations of the sum of azaarenes and the sum of the con-
centration of their metabolites close to the coast and lower concentrations further offshore. The concen-
trations of azaarenes and their metabolites are in the same order of magnitude as those found to induce
phototoxicity to algae.

The concentrations of mineral oil and PAHs in the surface sediments of the Dutch coastal zone of the
North Sea were, at most locations, above the Dutch chemical targets for environmental protection. Spatial
distribution of PAHs and mineral oil were slightly different from those of azaarenes and transformation
products.

Simultaneous GC–MS for azaarenes and their degradation products is possible but extraction/clean up
can be further improved. Azaarenes as well as their primary metabolic products are present in the marine
environment. In sediments the cumulative concentrations of transformation products amount to about
four times the cumulative concentrations of the azaarenes. In conclusion, azaarenes and their metabolites
constitute a new group of emerging polycyclic aromatic compounds which need more attention in the
future.

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concentrations are lower (1–10%) than those of the PAH analogues (Kozin et al., 1997; Bleeker et al., 1998). However, as the azaarenes are more water-soluble than PAHs they are likely to be more bioavailable (Pearlman et al., 1984). An unknown part of the azaarenes is biologically and photochemically oxidized into azaarones in the aquatic environment (Wiegman et al., 2001). De Voogt et al. (1999) concluded that keto-metabolites are major products in the aquatic fate of benzoquinolines. In the atmosphere similar photochemical transformations have been observed (Negrón-Encarnación and Arce, 2007). In contaminated groundwater hydroxylated N-heterocyclics have been reported to be significantly higher than their parent compounds (Pereira et al., 1988; Reineke et al., 2007).

Compared to azaarenes, much more scientific attention has been paid to the possible negative effects of PAHs on organisms (Gissel-Nielsen and Nielsen, 1996; Reynaud and Deschaux, 2006). PAHs have been found nearly everywhere in the aquatic environment (Jones et al., 1989; Wild and Jones, 1995; de Maagd, 1996; Xue and Warschovsky, 2005; Reynaud and Deschaux, 2006) and associated with the occurrence of for instance fish diseases (Vethaak et al., 1996).

A few papers have described the acute and chronic toxicity of azaarenes to several fish species, a few aquatic invertebrates, and marine algae (Gissel-Nielsen and Nielsen, 1996; Wiegman et al., 2001; Neuwöhner et al., 2008). Wiegman et al. (2001) showed that some of the oxidized derivatives of azaarenes are easily produced photochemically in the aquatic environment and that the derivatives are more toxic to algae than the parent compounds.

The experimental toxicological findings described above prompted an investigation into the environmental occurrence of these compounds. This paper describes the assessment of the concentrations of azaarenes and azaarones (ranging from two- to four-ringed structures) in the surface sediments of the Dutch coastal zone of the North Sea. For that purpose an analytical method was developed that would be able to detect both azaarenes and their oxygenated transformation products in one analytical run. Simultaneously the concentrations of PAHs and mineral oil in these sediments were determined in order to possibly relate their presence to that of the azaarenes.

2. Materials and methods

2.1. Solvents and chemicals

Kieselguhr GR (Merck, Darmstadt, Germany) was used as received. Aluminiumoxid 90 (Merck) aktiv neutral aktivitätstufe I. (0.063–0.200 mm, mesh 70–230) was dried overnight in an oven at 200 °C and deactivated with distilled water before use. Silica (Kieselgel 60, 70–230 mesh; Merck) was activated at 160 °C overnight and deactivated with distilled water.

All solvents used were of HPLC grade. Anhydrous sodium sulphate (Sigma–Aldrich Zwijndrecht, The Netherlands) was of analytical grade quality. Nitrogen-containing analytes were obtained from Sigma–Aldrich, and had purities varying between 97% and 99%. Acridine may contain acridinone and was further purified by adsorption chromatography on aluminium oxide. Homocyclic PAHs were obtained from various suppliers and all had a declared purity of 98–99%.

2.2. Sampling

Earlier studies on the distribution of metals and organic compounds (PCBs and PAHs) in the surface sediments (fraction < 63 μm) of the Dutch coastal zone revealed that the first 30–40 cm of the surface sediments are homogeneously mixed (Laane et al., 1999). The fraction smaller than 63 μm was isolated because most of the hydrophobic chemical compounds are adsorbed on the smaller particles. Standardization of concentrations is necessary because in the Dutch coastal zone there is a gradient in the amount of smaller particles in the surface sediment (Elisma, 1993). Klamer et al. (1999) showed that the fraction < 63 μm could be used to standardize the concentration of the various hydrophobic chemical compounds. Sixty-two surface samples (<20 cm) were sampled with a box core in the Dutch coastal zone of the North Sea from September 2000 to January 2001 (Fig. 1). Sampling locations are clustered into four groups: A (n = 8) and B (n = 10) off the Dutch mainland coast, C off the island of Texel (n = 20) and D near the island of Terschelling (n = 24) (Fig. 1). The locations A and B represent transects through the major salinity and suspended matter gradients along the Dutch coast. Locations C and D were part of a larger survey that investigated relationships between occurrence of organotin concentrations in marine sediments and shipping activities along the coast. It is known that sediment concentrations of various organic contaminants do not show large seasonal variations and therefore all locations were sampled once in time.

Sediment samples were stored at −20 °C and sieved over a 2 mm sieve before the fraction smaller than 63 μm was isolated by sieving and continuous flow centrifugation (Laane et al., 1999). The sediments can be characterized as sandy (<63 μm) with relatively low organic carbon contents (Fig. 2).

2.3. Analysis

Limits of detection were defined as three times the standard deviation of the noise level. LODs may vary from sample to sample, even for the same analyte, because of different sample intakes, and different signal to noise ratios caused by sample matrices. Seven azaarenes: quinoline (limit of detection: 4.0 ng g⁻¹), acridine (LOD: 4.2 ng g⁻¹), phenanthridine (LOD: 0.7 ng g⁻¹), 5,6-benzoquinoline (LOD: 4.4 ng g⁻¹), 7,8-benzoquinoline (LOD: 4.4 ng g⁻¹), benzo[a]acridine (LOD: 4.4 ng g⁻¹), benzo[c]acridine (LOD: 4.0 ng g⁻¹) and five oxidized derivatives: 2-, 5-, 6- and 8-hydroxy-quinoline (LOD: respectively, 4 (for samples from clusters C and D) and 10 (for samples from clusters A and B), 10, 0.5 and 11 ng g⁻¹) and 6(5H)-phenanthridinone (LOD: 3.9 ng g⁻¹) have been extracted and analyzed.
It appeared that three azaarenes, viz., 4-OH-acridone, 8-hydroxyquinoline and 4-hydroxyquinoline, could not be quantified (see below).

The molecular structures of the azaarenes and azaarones are given in Fig. 3.

For the determination of azaarenes and their derivatives, wet sediment (3–5 g, fraction < 63 μm) was mixed with Kieselguhr until a homogeneous free-flowing powder was obtained. One hundred microliters of an internal standard solution were then added and the sample was left to equilibrate (>1 h). Next, the sample was transferred to a glass Soxhlet thimble and extracted in a Soxhlet extractor. Pure solvent-washed sand was added to the tubes as filler (excitation 254 nm, detection at fluorescence maximum).

Recoveries of extraction and clean up procedure were evaluated by spiking analytes onto dried sediments for which analyte levels had been previously determined. If native levels were present then these values were subtracted from the recovered amounts.

A purified extract of sediment or a concentrated extract of water was analyzed by GC–Electron Impact-single quadrupole MS (Trace GC Ultra, Thermo Scientific) in SIM mode using a 50 m × 35 μm film thickness DB-wax column and on-column injection. Helium was used as carrier gas and the oven temperature was programmed from 70 °C (2 min hold) to 150 °C at t = 10 min and to 250 °C at t = 35 min (10 min hold). Deuterated standards of acridine and quinoline were used as surrogate standards. For the other azaarenes no D-standards were available. Ions used for identification and quantification are listed in the Supplementary information together with typical chromatograms of a sample and a standard of 8-OH-quinoline and a mass spectrum. All D-standards used were of 99% purity or better. For the identification of analytes in the samples a decision scheme was used as shown in the Supplementary information.
nitrogen flow. Analysis of mineral oil took place on a Chrompack CP9000 GC with FID and on-column injection (0.5 lL). The mineral oil concentration was calculated by integrating the part between C10 and C40, an external certified standard and dry solid extraction. The frozen samples were freeze-dried and ground by a ball mill before the organic carbon content was determined by combustion in an oxygen atmosphere, thus converting any organic carbon present to CO₂, and determining the CO₂ content by non-dispersive Infrared detection.

3. Results and discussion

3.1. Analytical method

In this study an analytical method was optimized and employed to simultaneously determine azaarenes and their oxygenated derivatives in a single GC–MS run. Method optimization included selection of MS fragment ions for confirmation (see Supplementary material), selection of extraction solvent, and determination of optimum volumes of clean-up fractions. We used different methods for extracting PANHs compared to PAHs because the PAH method (ASE) was an existing procedure validated for PAHs that had been shown previously in our laboratory to be more efficient (in time and volume consumption) than the Soxhlet extraction, whereas the extraction of PANH in our laboratory had been validated for the Soxhlet procedure only. Extraction solvents tested for PANH in a Soxhlet set up included n-hexane:acetone (1:1 v:v), hexane–EtAc (8:2), and methanol. Hexane–EtAc acetate yielded the best results, in particular for the azaarenes because of their limited solubility in other organic solvents (de Voogt et al., 1999). Koci et al. (2007) have tested different extraction methods for PANH spiked in soil and found Soxhlet extraction to be somewhat inferior to e.g. SFE or pressurized solvent extraction (ASE). However, the solvents they used are less suitable for the PANH transformation products. In this study we did not avail of SFE, and we are currently proceeding with testing efficiency of ASE for extraction PANH transformation products from sediments.

The clean up elution scheme was optimized by varying solvent amounts used for each fraction. The final fraction volumes selected (indicated in Section 2) were found to provide a suitable separation of analyte and waste fractions. The waste fractions were discarded so as to minimize presence of sample matrix components in the final extracts.

To the best of our knowledge this is the first time that simultaneous determination of azaarenes and their metabolites in sediments by GC–MS without a derivatization step has been reported. With HPLC coupled to DAD or fluorescence detection good separation of NPAH have been reported (see e.g. Svabensky et al., 2007), but so far no transformation products have been included. The simultaneous method turned out to work particularly well for the
parent compounds, 2-OH-quinoline and both metabolites of the three-ringed azaarenes, with overall recoveries >70%. The overall recoveries and a typical chromatogram are shown in the supporting information.

Obviously for some of the hydroxylated quinolines this methodology was suboptimal, leading to non recoveries for 8-OH-quinoline and 4-OH-quinoline, and also 4-OH-acridine. These compounds could not be quantified therefore. In the case of 5-OH quinoline and 6-OH-quinoline relatively low (5% and 18%, respectively), but consistent and repeatable recoveries were found (see supporting information). Both compounds could be quantified therefore, although these results should be taken as tentative. Probably in the case of 8-OH, 5-OH and 6-OH-quinoline the aluminum oxide absorption chromatography step retains most, or all of the analytes. In the course of this study no further optimization of the eluting solvent could be made. However, employing a more polar solvent, e.g. methanol–dichloromethane would probably recover the hydroxylated metabolites. A drawback would be the incompatibility of the resulting methanol extract with GC, requiring additional solvent exchange. In the case of 4-OH-quinoline, also no chromatographic separation could be obtained, i.e. very poor peak shapes were invariably observed, possibly partly caused by its possible tautomerism. Therefore quantification was not possible even if recoveries would have been better.

Analytical results presented below have not been corrected for recovery.

We also analyzed azaarenes and their transformation products in marine and fresh waters by the method described above. The levels observed were in general below the limits of detection.

3.2. Azaarenes and azaarones

The oxidized derivatives of quinoline, 2-hydroxyquinoline and 5-hydroxyquinoline, were present in the highest concentrations in the Dutch coastal zone of the North Sea; ranges were 7.4–980 ng g\(^{-1}\) (mean 132 ± 208 ng g\(^{-1}\), n = 28) and 12–188 ng g\(^{-1}\) (mean 60.5 ± 48.8 ng g\(^{-1}\), n = 31), respectively. The mean concentration of the parent compound quinoline was 11.7 ± 20.6 ng g\(^{-1}\) (range 0.97–66.4 ng g\(^{-1}\), n = 44). The highest concentrations of 2-hydroxy-quinoline and of 5-hydroxyquinoline were found in clusters D and A, respectively. Standardized on organic carbon the concentrations of these two compounds at the locations in cluster D were of the same order of magnitude as those in clusters B and C. At 21 sampling locations both concentrations were above the LOD and the ratio between 2-hydroxyquinoline and 5-hydroxyquinoline was not constant and ranged between 0.1 and 35. The mean ratio of 2-hydroxyquinoline to quinoline observed in this study amounts to 12. Values of between 1 and 30 have been reported for the ratio of 2-OH-quinoline to quinoline in contaminated groundwaters (Reineke et al., 2007).

The range in the concentrations of 6-hydroxyquinoline was somewhat lower: 4–16 ng g\(^{-1}\) (mean 9.9 ± 5.2 ng g\(^{-1}\), n = 4).

The concentrations of acridine in the sediments varied between 9.97 and 63.5 ng g\(^{-1}\) (mean = 30.3 ± 15.2 ng g\(^{-1}\); n = 48). Its transformation product 9(10H)-acridone was detected only at one sampling station where it amounted to 11.2 ng g\(^{-1}\).

The concentrations of 7,8-benzoquinoline were below the LOD at all sampling locations. The concentrations of 5,6-benzoquinoline and of 6(5H)-phenanthridinone varied between 3.9–10.8 ng g\(^{-1}\) (mean 6.4 ± 2.8, n = 5) and 4.2–28 ng g\(^{-1}\) (11.6 ± 4.3 ng g\(^{-1}\), n = 37), respectively. The concentration of phenanthridine was below its limit of detection at 0.7 ng g\(^{-1}\) at all sampling locations.

This absence of phenanthridine and the presence of acridine as well as both the 3-ring metabolites may be explained by the differences in transformation rates of phenanthridine and acridine. Van Herwijnen et al. (2004) showed that bacterial transformation rates of azaarenes depend on the concentration of the azaarene, and that at relatively low concentrations (as is the case in the present study) phenanthridine may be transformed more rapidly than acridine.

The concentrations of benzo[a]acridine and benzo[c]acridine, ranged between 3.76–24.8 ng g\(^{-1}\) (10.1 ± 5.6 ng g\(^{-1}\); n = 29) and 3.3–11.2 ng g\(^{-1}\) (5.6 ± 2.0 ng g\(^{-1}\); n = 22), respectively.

In 41 samples, the concentrations of both quinoline and the sum of the hydroxyquinolines were above the limit of detection. In all samples the summed concentration of the hydroxyquinolines was higher than that of quinoline (ratio of means: ~20). Only in four samples in cluster D the concentration of quinoline was higher than the hydroxyquinolines.

A gradient was found in the mean concentrations of quinoline and mean total concentrations of hydroxyquinolines going from lowest concentrations in location cluster D (39.6 and 55.9 ng g\(^{-1}\), respectively), via C (97.0 and 77.9 ng g\(^{-1}\), respectively), and B (161.6 and 157.9 ng g\(^{-1}\), respectively), to the highest concentrations observed in cluster A (335.43 and 332.0 ng g\(^{-1}\), respectively). A similar, but less steep, gradient was observed in the oxidized phenanthridines: 9.9 ng g\(^{-1}\) in cluster D, 11.37 ng g\(^{-1}\) in C, 13.15 ng g\(^{-1}\) in cluster B and 13.71 ng g\(^{-1}\) in cluster A. As an example, the gradients in the concentration of quinoline and of the sum of the oxidized quinolines along two transects in the Dutch coastal zone (see Fig. 1) are given in Fig. 4. Concentrations below the detection limit were set to zero.

The concentrations of azaarenes and azaarones observed in this study have been compared with concentrations found elsewhere (Table 1). The total azaarenes concentrations in the surface sediments of the Dutch coastal zone are somewhat less than those observed in the estuarine sediments of the Mersey and the sediment of Lake Zurich. Concentrations of acridine in this study are in the same order of magnitude of those found in Puget sound and higher than those reported in the Danshuei river in Taiwan.
concentrations of benzacridines and total benzoquinolines are of the same order of magnitude as found in other areas (Table 1).

3.3. Mineral oil

The mineral oil concentrations in surface sediments in the Dutch coastal zone of the North Sea ranged between <107 and 753 μg g⁻¹. The mineral oil concentration at transects A and B are presented in Fig. 5. The average concentration is higher at transect A than at B. At transect A the highest concentrations of mineral oil are found 6 km offshore, decreasing to lower values at 20 km. The concentration of mineral oil at transect B was below the limit of detection (<107 μg g⁻¹) at 10 km and further offshore. The concentrations of mineral oil observed at transects A and B (1–10 km offshore) in 2000 are similar to those reported in 1996 (Laane et al., 1999; Hegeman and Laane, 2004). The median concentration of mineral oil in the offshore samples of cluster D is 212 μg g⁻¹, whereas nearer to the shore a mean value of 133 μg g⁻¹ was found.

3.4. PAHs

Concentrations of the sum of the 16 EPA PAHs (Σ16 EPA) and the sum of the Borneff PAHs (Σ6 Borneff) ranged between 125.7–1134 ng g⁻¹ (average = 492.7 ng g⁻¹; n = 62) and 77.8–644 ng g⁻¹ (average = 285.7 ng g⁻¹; n = 62), respectively. The gradients in the concentrations of the Σ16 EPA and Σ6 Borneff PAHs at transects A and B in the Dutch coastal zone are presented in Fig. 6. The highest PAH concentrations were found at the two transects A and B in the area close to the coast (<15 km). Concentrations decrease at the locations more offshore. These values and gradients are in agreement with the PAHs concentrations found in that area in 2000 and 2003 (Hegeman and Laane, 2004; Van Gils, 2007).

The concentrations of the 2-ring compound naphthalene in the surface sediments of the Dutch coastal zone of the North Sea (fraction < 63 μm) was below the LOD at all stations. As shown above, the concentration of the heterocyclic 2-ring azaarene quinoline and of the oxidized quinolines were above detection limit at various locations. Phenanthrene was found in detectable concentrations at

![Fig. 5. Mineral oil concentration (mg kg⁻¹) in the surface sediments (fraction < 63 μm) at two transects (A, top and B, bottom, see Fig. 1) in the Dutch coastal zone of the North Sea. Note different distance and concentration scales in both panels.](image1)

![Fig. 6. Concentration of polycyclic hydrocarbons (PAHs; ng g⁻¹) in the surface sediments (fraction < 63 μm) at two transects A and B in the Dutch coastal zone of the North Sea (●: 16 EPA PAHs, ■: 6 of Borneff). Note different distance scale in both panels.](image2)
all locations in the Dutch coastal zone of the North Sea: its concentration ranged between 12 and 140 ng g⁻¹ (average = 53.3 ng g⁻¹).

As described above, the concentration of its heterocyclic analogue, phenanthridine, were below the LOD and the concentrations of the oxidized phenanthridines, 5,6-benzoquinoline and of 6(5H)-phenanthridinone (range between 8.2 and 38.8 ng g⁻¹) are in the same order of magnitude as those of the parent homocyclic PAH phenanthrene.

The concentrations of anthracene (range 1.9–35 ng g⁻¹, average 9.42 ng g⁻¹; n = 62) were below the concentrations found for the sum of the heterocyclic analogues acridine and its derivative 9(10H)-acridone (21–63 ng g⁻¹, average 31 ng g⁻¹). The concentrations of benzo[a]anthracene in the Dutch coastal zone of the North Sea (range between 7.98 and 82 ng g⁻¹, average 30.5 ng g⁻¹; n = 62) were somewhat higher than the sum of the heterocyclic analogues of benzo[a]anthracene, viz., benzo[a]acridine and benzo[c]acridine (range between 7 and 36.1 ng g⁻¹, average 15.4 ng g⁻¹).

It can be concluded that the sum of the concentrations of the azaarenes and azaarones range from almost equal to up to one order of magnitude higher than their homocyclic analogues.

As already stated, the concentrations of the oxidized derivatives of quinoline are higher than the concentration of the parent compound quinoline. Along the transects A and B the concentrations of quinoline are rather constant. For transect A the highest concentrations of the oxidized derivatives of quinolines are found around 6 km off shore. At transect B, the highest concentrations of oxidized quinolines are found also in the first kilometers offshore.

In general, concentrations of chemical substances in the first 10 km of transect A are strongly influenced by dumping of dredged material from the Rotterdam harbors and by the export of riverine material from the Rhine and Meuse (Laane et al., 1999, 2006). The spatial gradients observed for the concentrations of PAH and oil in this area are in agreement with these general observations. For PAH this has been established quantitatively by Van Gils (2007); the relative contribution from the rivers and dumping of dredged material to the total PAH concentration in the Dutch coastal zone is between 30% and 50% (Sonneveldt and Laane, 2001).

Although for most of the detectable concentrations of azaarenes and azaarones the concentrations are highest in the Dutch coastal zone, the observed spatial gradients differ from those of PAH and mineral oil. For quinoline this could be caused by its oxidation to hydroxyquinolines with the remaining low level of quinoline representing a non-available threshold concentration as found also at transects C and D. A comparable situation is found for acridine, with non-significant differences in the concentrations found at all locations. The levels of phenanthridine in marine sediments are below its LOD, the latter being probably higher than a possible threshold concentration of phenanthridine.

4. Conclusions

We conclude that simultaneous GC–MS for azaarenes and their degradation products is possible albeit that extraction and clean up can be further improved. In marine and fresh water levels of azaarenes and their transformation products are generally below the limits of detection. Azaarenes and azaarones have been detected for the first time simultaneously with a GC–MS method in relatively high concentrations in the surface sediments of the Dutch coastal zone. Detectable concentrations of azaarenes and azaarones ranged from 3.3–63 and 7.4–949 ng g⁻¹, respectively. Almost invariably the cumulative concentrations of the transformation products (azaarones) were higher than the cumulative concentrations of the parent compounds (azaarenes). The concentrations of the azaarenes and azaarones together are comparable with those of the PAHs and with levels that induce phototoxicity in algae.

Spatial concentration patterns of the azaarenes and azaarones slightly differ from those of total oil and PAHs in the Dutch coastal zone. Further monitoring of the emerging transformation products of azaarenes is warranted.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.04.029.

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