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Environmental Pollution 151 (2008) 53–59

ENVIRONMENTAL POLLUTION

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Organic pollutants in paper-recycling process water discharge areas: First detection and emission in aquatic environment

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Received 7 November 2006; received in revised form 26 February 2007; accepted 12 March 2007

This study reports the first detection of aryl hydrocarbons used in thermal paper in the environment.

Abstract

In this study, eight compounds have been identified and quantified from the samples collected from paper-recycling process water discharge areas. In particular, five aryl hydrocarbons, including a novel chlorinated aryl ether, were identified for the first time as environmental pollutants. In the effluent stream, concentration levels of up to 1600 μg L^{-1} and 190 μg g^{-1} were detected in the surface water and surface sediment, respectively. The results of this study have raised concerns regarding the organic chemicals used in thermal paper and the environmental consequences of their release.

Keywords: Aryl hydrocarbons; Surface sediment; Synthesis; Thermal paper; Paper-recycling process water

1. Introduction

Thermal paper has been widely used in an increasing number of applications such as point-of-sale receipts, admission tokens, ticket vending machines, medical records, baggage tags, fax papers, and food delivery in point-of-sale systems (Minami et al., 1991; Zeira and Ellett, 2000). In Japan, the annual production of special paper including thermal paper is approximately 132,000 tons (Japan Paper Association, 2005). In thermal paper manufacturing, large amounts of chemicals are used to achieve a higher recording sensitivity or to improve the preservability of recorded images (Iida and Tsuchida, 1999). Many of these chemicals are hydrophobic organic compounds such as aryl hydrocarbons and ethers (Kiritani et al., 1974; Jin et al., 2006; Mitsuo and Iwasaki, 2004; Norbäck et al., 1988). Moreover, most of these compounds are considered potentially persistent because of their structural analogy to polycyclic aromatic hydrocarbons (PAHs) and biphenyls. However, the environmental occurrence of these organic pollutants, which were not considered for a long time, is due to an increase in the production of thermal paper over the last decade.

The effluents and process waters from paper-recycling industries are complex matrices containing several compounds that may affect vertebrate physiology and reproductive functions (Mellanen et al., 1996; Meriläinen et al., 2006; Orrego et al., 2005; Rigol et al., 2004; Sepúlveda et al., 2003). For example, pulp and paper mill effluent was shown to exhibit significant estrogen and aryl hydrocarbon receptor (AhR) mediated activity in vivo when extracted with methanol (Parks et al., 2001; Zacharewski et al., 1995). In this study, however, AhR ligands were not identified by chemical analysis because of the lack of appropriate standards.

Therefore, the objective of this study was to identify a gas chromatography-mass spectrometry (GC-MS) method and authentic synthetic standards by using fractionation by gel permeation chromatography (GPC). This study reports on the first detection of aryl hydrocarbons and ethers in the surface water and surface sediment collected from paper-recycling process

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doi:10.1016/j.envpol.2007.03.012

water discharge areas. In addition, the proposed authentic synthetic standards would facilitate further analytical and toxicological studies of this environment.

2. Materials and methods

2.1. Chemicals

1,1′-Ditolylmethane (**1**) and *m*-terphenyl (**5**) were purchased from Wako Pure Chemical Industries, Osaka, Japan; 2,6-diisopropylnaphthalene (**3**) and 4-benzylbiphenyl (**8**), from Tokyo Chemical Industry, Tokyo, Japan; Methanol-d_4, from Cambridge Isotope Laboratories, Maryland, USA; chloroform-*d*, from Acros Organics, Tokyo, Japan; pyrene-d_{10}, from Kanto Chemicals, Tokyo, Japan; silica gel 60 (0.040–0.063 mm, for column chromatography), from Merck, Darmstadt, Germany; and Sephadex™ LH-20, from Amersham Biosciences, Tokyo, Japan. The solvents used were HPLC grade and were not purified further.

2.2. Synthesis and characterization

1,1′-Ditolylethane (**2**), 1,2-bis(3-methylphenoxy)ethane (**4**), benzyl 2-naphthyl ether (**6**), and 1-(4-chloro-3-methylphenoxy)-2-(3-methylphenoxy)ethane (**7**) were synthesized and characterized by proton nuclear magnetic resonance spectrometry (^{1}H NMR) spectroscopy at 500 MHz (JEOL ECA-500 spectrometer, JEOL, Tokyo, Japan), GC (HP6890A GC system, Agilent Technologies, Tokyo, Japan)-MS (JMS-AMSUN200, JEOL, Tokyo, Japan), and high-resolution fast atom bombardment (FAB+) MS (JMS-700 instrument, JEOL, Tokyo, Japan).

Compound (**2**) was obtained by coupling toluene and acetaldehyde with sulfuric acid as the catalyst (Innes and Occelli, 1985). Toluene (4.1 mL) in concentrated sulfuric acid (1.5 mL) was cooled in an ice bath, and acetaldehyde (0.6 mL) was added over a period of 30 min. This mixture was stirred for 3 h at 5 °C, poured into ice-water, and extracted using ethyl acetate. The organic solution was washed with brine and dried over sodium sulfate. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column (500 × 30 mm) and eluted with hexane/ethyl acetate (8/2, v/v). Fractions containing compound (**2**) were collected and the solvent was evaporated to yield a colorless liquid (70 mg). ^{1}H NMR ($CDCl_3$): δ 1.60 (d, 3H, CH_3), 2.29 (s, 6H, 2 × CH_3), 4.07 (q, 1H, CH), 7.07 (d, 4H, $J = 7.45$ Hz, Ar-H), 7.09 (d, 4H, $J = 7.45$ Hz, Ar-H); MS: 210 (M^+).

Compound (**4**) was obtained by reacting *m*-cresol in the presence of 50% aqueous sodium hydroxide. Fifty percent aqueous sodium hydroxide (10 mL) was added to a solution of *m*-cresol (50 g) in 1,2-dichloroethane (20 mL) over a period of 60 min at 105 °C, and the mixture was then refluxed for 7 h. After cooling, the reaction mixture was extracted with ether. The organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated to yield compound (**4**) (15 g), which was crystallized from ethanol; the mp of the compound was 96–97 °C (lit. 98 °C, Satomura et al., 1986). ^{1}H NMR ($CDCl_3$): δ 2.33 (s, 6H, 2 × CH_3), 4.30 (s, 4H, 2 × CH_2), 6.74–6.80 (m, 6H, Ar-H), 7.17 (t, 2H, $J = 8.05$ Hz, Ar-H); MS: 242 (M^+).

Compound (**6**) was obtained by ether synthesis of 2-naphthol and benzyl bromide. The mixture of benzyl bromide that was prepared from toluene (9.2 g) and bromine (15 g) under light irradiation, 2-naphthol (11.5 g), potassium carbonate (11 g), and acetone (150 mL) was refluxed for 24 h. Water (100 mL) was added to this mixture and it was extracted with ether. The extract was washed with 10% aqueous sodium hydroxide after washing with brine and dried over sodium sulfate. The solvent was evaporated to yield compound (**6**) (6.1 g), which was crystallized from ether; the mp of the compound was 98–100 °C (lit. 99–100 °C, Kornblum et al., 1963). ^{1}H NMR ($CDCl_3$): δ 5.19 (s, 2H, CH_2), 7.23 (s, 1H, Ar-H), 7.25 (d, 1H, $J = 2.30$ Hz, Ar-H), 7.33–7.46 (m, 5H, Ar-H), 7.50 (d, 2H, $J = 7.45$ Hz, Ar-H), 7.73 (d, 1H, $J = 8.60$ Hz, Ar-H), 7.76 (d, 1H, $J = 8.60$ Hz, Ar-H), 7.78 (d, 1H, $J = 7.45$ Hz, Ar-H); MS: 234 (M^+).

Compound (**7**) was obtained by reacting compound (**4**) (0.24 g) with chloramine T (2.8 g) in a refluxing 50% aqueous dioxane solution (10 mL) for 4 h. Water (10 mL) was added to this mixture and it was extracted with ethyl acetate. The organic solution was washed with brine and dried over sodium sulfate. After the removal of the solvent under a reduced pressure, the obtained residue was chromatographed on a silica gel column (500 × 30 mm) and eluted with hexane/dichloromethane (7/3, v/v). Fractions containing compound (**7**) were collected and the solvent was evaporated to yield a white powder (0.17 g). ^{1}H NMR ($CDCl_3$): δ 2.34 (d, 6H, 2 × CH_3), 4.28 (d, 4H, 2 × CH_2), 6.71–6.83 (m, 5H, Ar-H), 7.17 (t, 1H, $J = 8.00$ Hz, Ar-H), 7.22 (d, 1H, $J = 8.60$ Hz, Ar-H); HR FAB MS +ve mode (M^+): 276.0856 (Int. 100%) (calcd. for 276.0888; $C_{16}H_{17}O_2^{35}Cl$), 278.0901 (Int. 42%) (calcd. for 278.0918; $C_{16}H_{17}O_2^{37}Cl$).

2.3. Sampling locations, sample collection, and physicochemical characterization

There are 85 pulp and paper mill and recycling paper mill industries in Fuji city, Shizuoka Prefecture, which is the largest paper mill industry area in Japan. The port is also a commercial ship harbor with a total traffic of 3700 ships in 2005 (Port of TAGONOURA Administration Office). The process water from these industries is discharged via an outfall into the port; the average daily flow is 570,000 $m^3\ d^{-1}$. Previous research has revealed that the chlorinated derivatives of bisphenol A originating from the wastepaper recycling plants were found in the effluents discharged into this outfall (Fukazawa et al., 2001).

The samples were collected in two months—November 2005 and August 2006—from the outfall (site 1), upstream (site 2), mouth of the port (site 3), and two tributaries (sites 4 and 5) from which the rivers discharge into the Pacific Ocean (Fig. 1). Sediment samples (500 g) were collected from the sediment surface (depth: 5 cm) using an Ekman-Birge bottom sampler, and water samples (1 L) were collected from the surface water (depth: 10 cm) between 8 am and 10 am. The samples were collected in glass bottles with aluminum-lined stoppers, transported to the laboratory in cold boxes with ice, and stored at 4 °C until analysis (within 10 days). The physicochemical characterizations of the samples are listed in Table 1. The temperature and pH values were measured using a pH meter (PICCOLO+, HANNA instruments, Tokyo, Japan). The salinity was obtained by converting the conductivity values to salinity using an electrical conductivity meter (CM-14P, TOA Electronics, Tokyo, Japan). The total organic carbon (TOC) was measured using a TOC analyzer

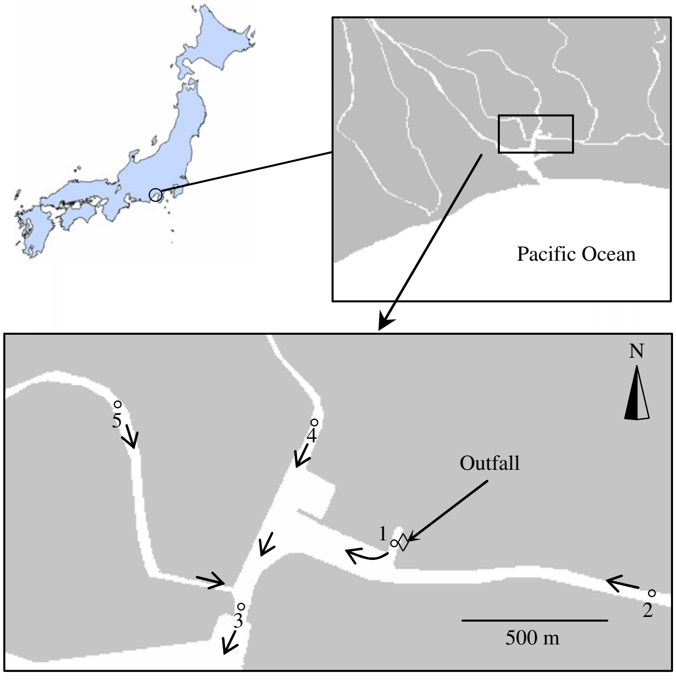

Fig. 1. Location of the sampling sites and the outfall in Shizuoka Prefecture. The arrows indicate the direction of water flow in the area.

Table 1
Physicochemical characterizations of the samples obtained from the study area

	Surface water						Surface sediment	
	Site 1	Site 2	Site 3	Site 4	Site 5	Blank	Site 1	Site 3
Temperature/°C	24	24	26	24	20	16	n.a.[a]	n.a.
pH	7.1	7.6	7.2	7.8	7.9	8.0	n.a.	n.a.
Salinity/%	0.05	0.02	0.30	<0.01	<0.01	<0.01	n.a.	n.a.
TOC[b]/%	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	21	12

[a] Not analyzed.

[b] Total organic carbon.

(TOC-5000A, Shimadzu, Kyoto, Japan) combined with an electric furnace (SSM-5000A, Shimadzu, Kyoto, Japan) after pretreatment with 1 M hydrochloric acid.

2.4. Extraction and fractionation

The freeze-dried sediment samples (10 g) were extracted by ultrasonic extraction using methanol (10 mL × 4). After the removal of the solvent under reduced pressure, the residues dissolved in the methanol (5 mL) and samples (1 mL) were subjected to gel permeation chromatography on a Sephadex™ LH-20/methanol column (300 × 30 mm) and 18 mL fractions were collected using a fraction collector (FR50N, Yamazen, Osaka, Japan). The methanol was removed separately from each fraction by using a stream of nitrogen. The fractions were pipetted along with methanol into a GC-MS vial and dried in a stream of nitrogen. The extracted samples were reconstituted into dichloromethane (0.1 mL) containing 2 μg mL^{-1} of the internal standard (pyrene-d_{10}) and examined by GC-MS.

Water samples (100 mL) were filtered (GF/A glass microfiber filters, Whatman Japan K.K, Tokyo, Japan) and extracted in dichloromethane (25 mL × 2) by using a shaker (Recipro Shaker SR-2s, TAITEC, Saitama, Japan) at 265 rpm for 10 min. After the removal of the solvent under reduced pressure, the residue was treated in the same manner as the sediment samples for the GC-MS examination.

2.5. Analytical methods

The standard and sample extracts were analyzed by employing GC (HP 6890 Series, Palo Alto, CA, USA)-MS (HP 6890 Series mass selective detector, Palo Alto, CA, USA) on a HP-5 fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film, J&W Scientific, Folsom, CA, USA). The column temperature was initially maintained at 60 °C for 1 min and it was then programmed to approach 280 °C at a rate of 10 °C min^{-1} with a final hold time of 7 min. Helium was used as the carrier gas with a flow rate of 1.0 mL min^{-1}, and the column head pressure was maintained at 8.0 psi. The injector temperature was maintained at 250 °C and the injection volume was 1.0 μL in the splitless mode. The electron multiplier voltage for MS was 1988 V, and the interface temperature was maintained at 280 °C. Mass spectra were obtained by electron impact ionization at a voltage of 70 eV and scanned in a range of m/z 50 to 550 a.m.u. at a rate of 1.5 scans s^{-1}; the ion source temperature was maintained at 250 °C. The chemicals in the samples were identified by comparing their gas chromatographic retention times and mass spectra with those of the authentic standards. These compounds were quantified by correlating the ratio of the peak area of the compound of interest to that of the internal standard (pyrene-d_{10}) to the calibration curve of the standard solution. The standard calibration solution containing compounds (**1**–**8**) was prepared in dichloromethane.

2.6. Quality assurance and quality control

Data are expressed as means of two separate experiments performed in duplicate. The characteristics of the method and chemicals used in this study are listed in Table 2. The partition coefficients for octanol and water have been calculated using the LogKow program (Syracuse Research Corporation, 2007). The relative standard deviations of these results were within 13% and 24% for the recoveries and samples, respectively. The recoveries were determined by using distillated water and pre-ignited sand spiked at 5 μg L^{-1} and 1 μg g^{-1}, respectively. The recoveries varied between 89% and 109%, and all standards exhibited linearity from 0.7 μg L^{-1} up to 64 μg L^{-1}. The coefficient of determination (R^2) ranged from 0.98 to 0.99 for five concentration levels. The concentration of the lowest calibration standard was operationally defined as the limit of quantification (LOQ). Blank samples (surface water

Table 2
Characteristics of the method and chemicals

Compound		R_t[a]	MS Ions		Recovery %		LOQ[b] μg L^{-1}	R^2[c]	LogKow[d]
		Min	Quant[e] m/z	Conf[f] m/z	Water	Sand			
1	4,4′-Dimethyldiphenylmethane	13.4	181	196	107	104	2.7	0.99	5.11
2	1,1-Di(4-methylphenyl)ethane	14.0	195	210	108	106	2.2	0.99	5.24
3	2,6-Diisopropylnaphthalene	14.2	197	212	108	109	0.8	0.99	6.08
4	1,2-Bis(3-methylphenoxy)ethane	16.9	242	134	100	96	0.6	0.98	4.90
5	*m*-Terphenyl	18.4	230	115	97	102	0.8	0.99	5.52
6	Benzyl 2-naphthyl ether	18.5	234	91	105	96	0.9	0.99	4.96
7	1-(4-Chloro-3-methylphenoxy)-2-(3-methylphenoxy)ethane	18.8	276	168	89	95	0.7	0.99	5.16
8	4-Benzylbiphenyl	19.1	244	165	96	97	1.2	0.99	5.78

[a] Retention time.

[b] Limits of quantification.

[c] Coefficient of determination.

[d] Calculated using SRC's LogKow (KowWIN) Program.

[e] For quantification.

[f] For confirmatory purposes.

from the Kusanagi river, E138°27′24″, N34°59′28″) were routinely analyzed and no contamination of solvents or equipment was detected.

3. Results and discussion

The typical chromatograms of the extracts from a surface sediment sample (site 3) that were fractionated by GPC on a Sephadex™ LH-20 are shown in Fig. 2. The MS data of the identified compounds in the sample and their standards are shown in Fig. 3. Four compounds identified as contaminants in the samples were synthesized and characterized (^{1}H NMR spectroscopy and mass spectrometry). Fractions 12–13 contained solvents used in the manufacture of thermal paper, such as diarylalkanes (**1** and **2**) and alkyl-substituted naphthalene (**3**) (García et al., 2006; Jin et al., 2006; Kiritani et al., 1974). Fig. 2a reveals that the fragmentation patterns of the spectra of all three peaks, including peak 2, on the total ion chromatogram were similar to that of an authentic sample of compound (**2**) and were therefore as its constitutional isomers. For similar reasons, all four peaks, including peak 3, on the total ion chromatogram were also characterized as the constitutional isomers of diisopropylnaphthalene (**3**). Fraction 14 contained an aryl ether (**4**), its chloro-derivative (**7**), and a non-fused tricyclic compound (**8**). Fraction 15 contained compound (**5**) and naphthyl ether (**6**) (Fig. 2b,c). Compounds (**4**)–(**6**) and (**8**) are widely employed as color sensitizers during the manufacture of thermal paper and carbonless copy paper (Iida and Tsuchida, 1999; Iwasaki et al., 2005; Makitalo and Mattila, 2006).

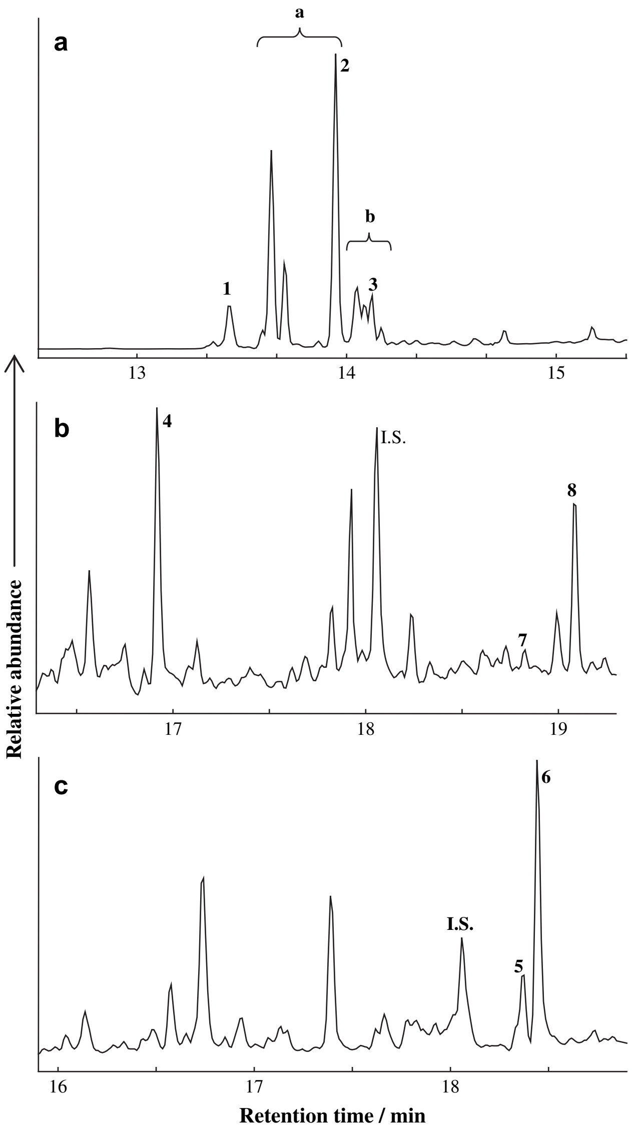

Fig. 2. Typical total ion chromatograms of fractionated extracts—(a) fraction 12; (b) fraction 14; and (c) fraction 15—from the surface sediment (site 3) that were obtained by gel permeation chromatography on a Sephadex™ LH-20. ^{a}The chromatogram of 1,1-di(4-methylphenyl)ethane isomers consists of three peaks. ^{b}The chromatogram of the diisopropylnaphthalene isomers consists of four peaks. I.S. = Internal standard.

Table 3 summarizes the concentrations of the aryl hydrocarbons and ethers present in the samples obtained from the study area. Higher concentrations were observed in site 1 because it is close to the outfall area of the industrial process water. Site 3, which is the mouth of the port, receives a combination of the waters from the outfall (site 4) and site 5. These compounds were also found in site 3, whereas they were not detected upstream (site 2) of the outfall and in the other two tributaries (sites 4 and 5). Therefore, the compounds detected at sites 1 and 3 suggest that the chemicals detected in the paper-recycling process water originated from thermal paper. The concentration levels in site 1 ranged from 1.2 to 1600 $\mu g\ L^{-1}$ and LOQ to 190 $\mu g\ g^{-1}$ for the water and sediment samples, respectively. At the downstream site of the outfall, the concentration levels ranged from LOQ to 8.9 $\mu g\ L^{-1}$ and LOQ to 53 $\mu g\ g^{-1}$ for the water and sediment samples, respectively. In particular, compounds (**2**), (**4**), and (**6**)–(**8**) were detected for the first time as environmental pollutants. Compound (**2**) was the most abundant in the samples investigated; its maximum measured concentration was comparable to that of alkylbenzenesulfonate found in paper-recycling process waters, as reported previously (5000 $\mu g\ L^{-1}$, Rigol et al., 2002). The concentrations of compounds (**1**) and (**3**) in the water near the outfall were 500 and 260 $\mu g\ L^{-1}$, respectively; these values are equal to those of bisphenol A found in process waters during papermaking (187 $\mu g\ L^{-1}$, Rigol et al., 2004). Compounds (**4**) and (**6**), which are aryl ethers, were found at levels of up to 10 and 23 $\mu g\ L^{-1}$, respectively. These concentration levels were similar to those stated in the literature data on nonylphenol in paper-recycling process waters (1–10 $\mu g\ L^{-1}$, Lacorte et al., 2003).

Several of the identified compounds are known as anthropogenic pollutants and are consequently reported in some environmental studies. Compound (**1**) has been observed in air particulates as soot originating from fuel (Jones et al., 2004). Compounds (**3**) and (**5**) were reported to be present in sediments as contaminants resulting from the emissions from biomass fuel combustion as well as manufacturing plants (Kawata et al., 2005). On the other hand, this study reports the presence of compounds (**2**), (**4**), (**6**), (**7**), and (**8**) in the aquatic environment. The emission of these compounds into the aquatic environment has not been reported thus far. Moreover, no data

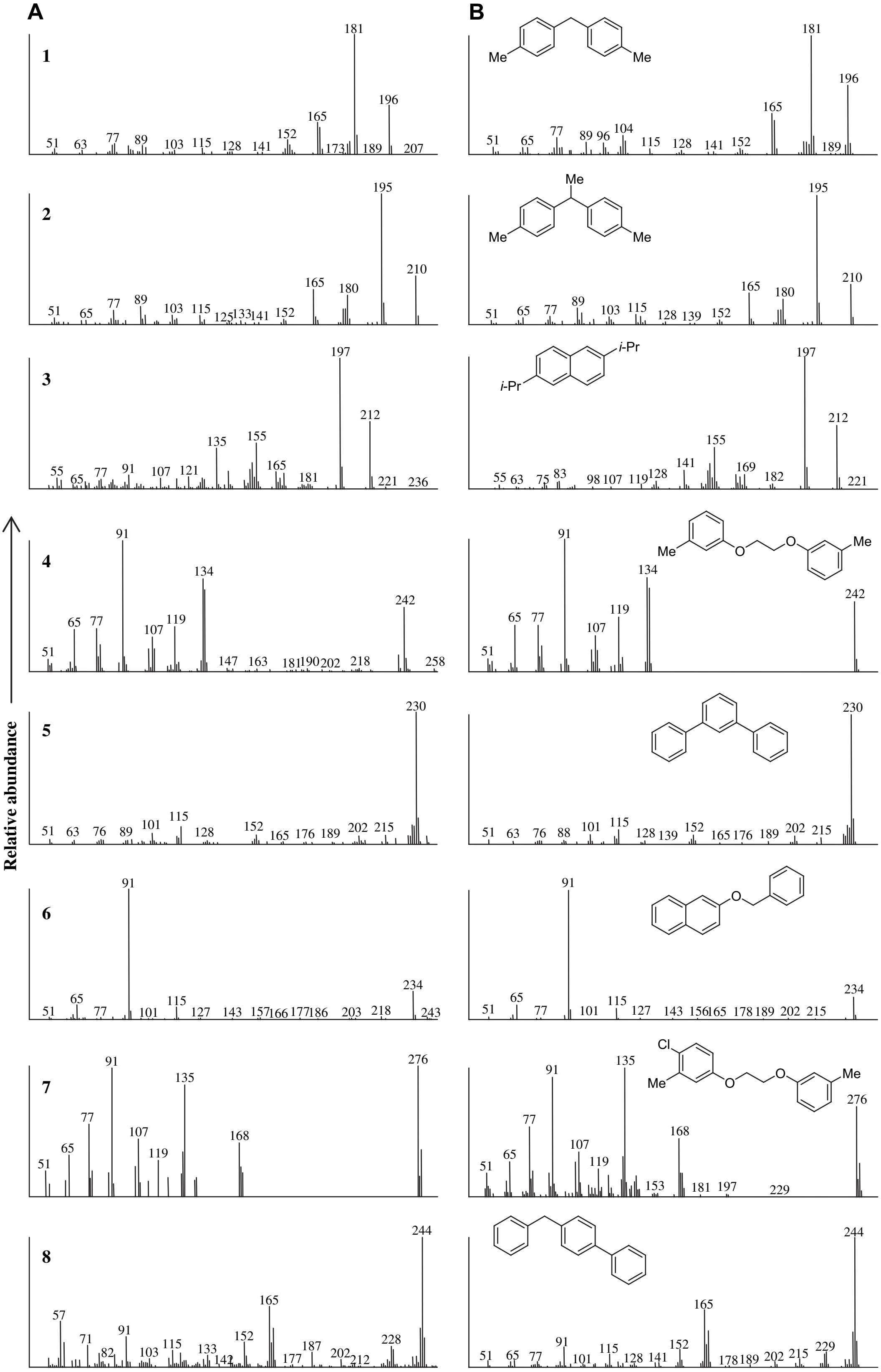

Fig. 3. Mass spectra of compounds (**1**–**8**) (A) in the surface sediment (site 3) and (B) of the authentic standards. Numbers refer to the peak numbers of Fig. 2.

Table 3
Concentrations of organic pollutants in the samples collected from the paper-recycling process water discharge areas

	Compound	Outfall watershed					Site 4	Site 5
		Adjacent area, site 1		Upstream, site 2	Downstream, site 3		Water $\mu g\ L^{-1}$	Water $\mu g\ L^{-1}$
		Water $\mu g\ L^{-1}$	Sediment $\mu g\ g^{-1}$	Water $\mu g\ L^{-1}$	Water $\mu g\ L^{-1}$	Sediment $\mu g\ g^{-1}$		
1	1,1′-Ditolylmethane	500	38	<LOQ[a]	4.1	5.9	<LOQ	<LOQ
2	1,1′-Ditolylethane	1600	190	<LOQ	8.9	53	<LOQ	<LOQ
3	2,6-Diisopropylnaphthalene	260	16	<LOQ	1.5	2.9	<LOQ	<LOQ
4	1,2-Bis(3-methylphenoxy)ethane	10	2.2	<LOQ	1.4	0.7	<LOQ	<LOQ
5	*m*-Terphenyl	8.3	1.5	<LOQ	1.2	<LOQ	<LOQ	<LOQ
6	Benzyl 2-naphthyl ether	23	3.7	<LOQ	1.7	1.2	<LOQ	<LOQ
7	1-(4-Chloro-3-methylphenoxy)-2-(3-methylphenoxy)ethane	1.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
8	4-Benzylbiphenyl	5.8	1.6	<LOQ	1.9	<1.2	<LOQ	<LOQ

[a] LOQ = limits of quantification.

have been published on the detection of color sensitizer metabolites. The results of this study raise concerns regarding the organic pollutants originating from thermal paper in the paper-recycling process waters. However, the results are merely preliminary and correspond to those of grab samples. In order to estimate the risks of these pollutants to aquatic organisms, further studies on the distribution and fate of the identified compounds and their toxicities should be conducted.

4. Conclusions

The GC-MS analyses revealed the presence of eight aryl hydrocarbons and ethers in the water and sediment samples collected from paper-recycling process water discharge areas. In particular, 1,1′-ditolylethane (**2**), 1,2-bis(3-methylphenoxy)ethane (**4**), benzyl 2-naphthyl ether (**6**), 1-(4-chloro-3-methylphenoxy)-2-(3-methylphenoxy)ethane (**7**), and 4-benzylbiphenyl (**8**) were identified for the first time as environmental pollutants. Concentration levels of up to 1600 $\mu g\ L^{-1}$ and 190 $\mu g\ g^{-1}$ were detected for the surface water and surface sediment samples, respectively. Compound (**2**) was the most abundant in the investigated samples; its concentration was comparable to that of alkylbenzenesulfonate found in paper-recycling process waters, as reported previously. The authentic synthetic standards and analytical studies reported in this study will further investigations regarding the environmental consequences of the release of the abovementioned pollutants.

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