

HS-SPME/GC–MS analysis of volatile and semi-volatile organic compounds emitted from municipal sewage sludge

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Abstract The aim of the research involved identification and semi-quantitative determination of unknown volatile and semi-volatile organic compounds emitted to air by sewage sludge formed in the process of municipal wastewater treatment in a sewage treatment plant. Samples taken directly after completion of the technological process as well as the sludge stored on the premise of the sewage treatment plant were analyzed. A simple method using off-line headspace solid-phase microextraction combined with gas chromatography–mass spectrometry has been proposed for extraction and detection of organic pollutants. For reliable identification of compounds, combination of two independent parameters: mass spectra and linear temperature programmed retention indices were employed. Over 170 compounds of different structure were identified including aliphatic and aromatic hydrocarbons, alcohols, esters, carbonyls, as well as sulfur, nitrogen, and chlorine containing compounds. The prevailing substances included: ethyl ether, *n*-hexane, *p*-xylene, *o*-xylene, mesitylene, *m*-ethylbenzene, limonene, *n*-decane, *n*-undecane, and *n*-dodecane. A few compounds such as methanethiol, dimethyl polysulfide, octaatomic

sulfur, phthalic anhydride, and indoles were identified in the sludge for the first time.

Keywords Sewage sludge · Organic compounds · HS-SPME · GC–MS

Introduction

Approached quantitatively, sludge formed in the process of wastewater treatment constitutes a few percent of waste products produced by human economic activity. However, due to the environmental threat, it poses makes sewage sludge management one of the most difficult problems in the majority of European countries. According to the policy of the European Council, the most desired solution to the problem of sewage sludge management is sludge recycling, i.e., its return to the environment with the use of natural methods, including agricultural activities. The indispensable condition of the implementation sludge recycling is to assure appropriate sludge quality including both biological (i.e., elimination of widely occurring in sludge pathogenic organisms, such as pathogenic bacteria, fungi, and eggs of human and animal parasites) as well as chemical purity.

Volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC) contained in sewage and sewage sludge can exert a harmful influence on the natural environment and human

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health. Certain groups of these compounds reach sewage treatment plants in the wastewater from households and industrial plants. Some of them undergo biodegradation during the process of sewage treatment; others remain in the sewage sludge in an unchanged form. A large number of VOCs and SVOCs are formed during decomposition of various organic compounds as well as during metabolism of microorganisms that form active sludge in biological sewage treatment plants. Due to their volatile character, some of these compounds escape to the atmosphere at different stages of sewage treatment processes (Simonich et al. 2000; Escalasa et al. 2003; Wu et al. 2006).

In the literature on the subject, only a small number of research papers has been devoted to the determination of volatile and semi-volatile organic compounds in the sewage sludge. Main VOCs identified in the sewage sludge are: *n*-alkanes, branched, cyclic, and unsaturated aliphatic hydrocarbons, aromatic hydrocarbons, and halogenated aliphatic hydrocarbons (Eitzer 1995; Wilson et al. 1996a, b; Pagans et al. 2006; Harrison et al. 2006; Koe and Shen 1997; Webber et al. 1996; Van Durme et al. 1992). Dimethyl sulfide, dimethyl disulfide, limonene, and α -pinene were identified as the most significant odorous VOCs in the wastewater sludge. Other compounds included: carbon disulfide (Eitzer 1995; Harrison et al. 2006), carbonyl compounds (Eitzer 1995; Wilson et al. 1996a), and some terpenes: camphene, 3-carene, terpineol (Eitzer 1995). The most frequently detected SVOCs in the sludges were: polycyclic aromatic hydrocarbons, phthalic acid esters, chlorobenzenes, nitroaromatic compounds, and phenols (Harrison et al. 2006; Cai et al. 2007).

Extraction and concentration of volatile and semi-volatile organic compounds from the samples of sludge were made with the use of sorption tubes filled up with Tenax, Carbotrap, or Carbosieve granulates (Eitzer 1995; Koe and Shen 1997). The sampling using sorbent tubes or traps requires complete retention during sampling as well as complete recovery during analysis. Quantitative monitoring of vapor-phase organics using sorbents could be made by active sampling onto tubes packed with one or more sorbents, passive sampling onto sorbents or cartridges or

whole air sampling methods (Matysik et al. 2009; Woolfenden 2010a, b; ISO EN 2000; ISO EN 2003; ASTM 1998; NSAI 2011; Kim et al. 2005). For the recovery of analytes from sorbents, two techniques: solvent extraction or thermal desorption are used (ISO EN 2000; ISO EN 2003; US EPA 1996). For the separation of VOCs and SVOCs from sludge samples, the “purge and trap” technique (Webber et al. 1996) and extraction with water-pentane mixture (Wilson et al. 1996b) are applied. The gaseous phase can also be taken directly with the help of a gas-proof syringe (Pagans et al. 2006). For the final determination the technique of gas chromatography coupled with the detection with the mass spectrometry technique (GC–MS) or with a flame ionisation detector (GC-FID) is performed.

In this work, to extract both VOCs and SVOCs from wastewater sludge, the SPME technique has been implemented. This technique, devised in 1987–1989 (Pawliszyn and Liu 1987; Arthur and Pawliszyn 1990) is a simple and effective extraction technique that eliminates the need of using solvents or complicated apparatus. To conduct SPME isolation, a relatively small sample is required and its preparation is quick. In direct immersion SPME (DI-SPME), the fiber is directly placed in the sample. In headspace SPME mode, the fiber is exposed to the vapor phase above the liquid or solid matrix. Headspace solid-phase microextraction (HS-SPME) is frequently used for isolation of volatile and semi-volatile compounds (Pawliszyn 1997). Desorption of compounds retained on the fiber may be conducted directly in a GC injector. Although this desorption manner may be loaded with some risk of introducing air to the system and a resultant loss of most volatile compounds, it is the most commonly used method due to its simplicity and no need to use additional equipment.

SPME is a microextraction technique, which means that the amount of extraction medium is very small compared to the sample volume. As a result, exhaustive transfer of analytes to the extracting phase, which is characterized by the retention of vapor-organics on sorbents, does not occur here. HS-SPME is a complex multi-phase partitioning system, where equilibrium is reached in two systems: between the sample matrix and

the headspace and between the headspace and the extracting phase. Temperature exerts a great impact on those processes. Also other experimental conditions greatly affect the course of the isolation process, e.g., extraction time, sample mixing, sample volume, headspace volume, pH, salting out effect, etc. Strict adherence to the procedures established for SPME technique is more important than equilibrium conditions during the extraction.

The HS-SPME technique has been widely used for the determination of VOCs and SVOCs present in various matrices. SPME, in combination with GC and HPLC, was reported to have been used for the analysis of VOCs and SVOCs in indoor air (Hippelein 2006), lower troposphere (Mangani et al. 2003), gaseous industrial effluents (Domeño et al. 2004), and human breath (Spinhirne et al. 2004). Volatile and semi-volatile organic compounds were extracted with the SPME technique also from water samples (Bravo-Linares et al. 2007) and biological samples: plant and animal tissues and organisms (Isidorov et al. 2005a, b; Villaverde et al. 2007), bacteria (Gu et al. 2007), and blood (Blount et al. 2006).

There are only a few papers dealing with the application of SPME to the analysis of organic pollutants in sludge samples. DI-SPME was used for the determination of nitrobenzenes, nitrotoluene, and triazines in sludge samples (Basheer and Lee 2004; Jönsson et al. 2007; Zeng et al. 2009). Synthetic polycyclic musks were extracted from sewage sludges by HS-SPME and microwave-assisted SPME (Llompарт et al. 2003; Wu and Ding 2010) during aliphatic primary amines isolation by pressurized hot water extraction followed by HS-SPME (Llop et al. 2010).

Experimental section

Sludge samples Samples of sludge were obtained from the Wastewater Treatment Plant located in Białystok. The plant receives municipal wastewater from the area of Białystok City—approximately 15 million cubic meters of wastewater are disposed to the plant in a year. The treatment process consists of mechanical and biological stages and lasts from 24 to 30 h. The sludge, being a by-product of the technological process of

the sewage treatment, is dehydrated and stored on a heap. The sewage sludge is composed of excessive active deposit mixed with suspension coming from the wastewater reaching the sewage treatment plant and stored in preliminary settling tanks. Sewage sludge samples were collected eight times between October 2006 and May 2007. The samples were collected from the dehydrating press to a glass container and analyzed immediately after collection.

VOC and SVOC sampling Isolation of VOCs was carried out with the help of SPME fibers with coating of Carboxene suspended in polydimethylsiloxane (CAR/PDMS, 75 μm) and fibers with dual coating of divinylbenzene and carboxene (50/30 μm) suspended in polydimethylsiloxane (DVB/CAR/PDMS) made by Supelco, USA. Extraction of VOCs and SVOCs was carried out in both laboratory and field conditions. In the first variant a hermetic glass container of 900 ml in volume fitted with inlet ports was filled with 150 g sludge with the addition of 700 ml of deionized water. Next, the SPME device fiber, previously conditioned according to manufacturer's recommendations, was inserted into the headspace above the sample. The extraction was carried out for 2.5 h at 20°C with mixing speed of 900 rpm. In the field conditions, the sampling of volatiles was carried out using poly(methyl methacrylate) chamber placed on the dehydrated sludge. The chamber was fitted with two inlet ports for SPME fiber and a fan ensuring continuous mixing of gases inside the chamber. The extraction was carried out on the heap situated in the area of the sewage treatment plant in Białystok, where the sludge is transferred after dehydration. The sludge transferred from the dehydrating press is continuously mixed with the sludge stored on the heap, which gives its entire volume the same properties. The sampling chamber was positioned on the surface of such averaged sludge. The sampling was conducted three times between November 2006 and April 2007; during experiments the air temperature ranged from 0°C to 10°C, the temperature of the sludge was ca. 20°C. The extraction was carried out for 2.5 h. After this time the SPME device fibers were protected with silicone septa and transferred to the laboratory, where the

analytes were instantly desorbed thermally in an injector of gas chromatograph and analysed using the GC–MS technique.

Instrumentation Gas chromatographic analyses were carried out using a HP 6890 gas chromatograph with electronic pressure control and with a mass selective detector HP 5973 (electron impact source and quadrupole analyzer) from the Agilent Technologies, USA. This device was equipped with split/splitless injector and HP-5MS column (5% phenylmethylsiloxane) size 30 m × 0.25 mm, i.e., coated with 0.25 µm film thickness. The scan frequency was 2.64 times per second and the mass range scanned was 28–600 amu. The carrier gas was helium (99.999%) at a constant flow rate of 1.0 ml/min. A splitless injection technique was used and injection port temperature of 250°C. The oven program was as follows: 35°C for 5 min, 3°C/min to 300°C, 300°C for 15 min. The electron impact source temperature was 230°C with electron energy of 70 eV. The quadrupole temperature was 150°C, and GC interface temperature was 280°C. The instrument was tuned on perfluorotributylamine.

Results and discussion

Table 1 contains a list of organic compounds extracted from the sewage sludge, as well as some analytical parameters used for identification, Chemical Abstracts Service Registry Number for each compound and information on the variant of determination, where a given compound has been identified. Exemplary chromatograms are presented in Fig. 1.

Before commencing our research, the amount of information concerning the composition of organic compounds contained in the sewage sludge was rather poor, due to the limited number of publications concerning this problem. Additionally, the composition of the sewage sludge depends on some local factors, such as the number and type of industrial plants connected to the sewage treatment plant and the management of wastewater treatment processes. Taking the above into account, the research was mainly focused on prospective analyses. To ensure correct

identification results, two independent parameters, i.e., mass spectra and linear temperature programmed chromatographic retention indices were applied.

Mass spectra recorded during the analyses were compared to spectra contained in the NIST MS base. Using the equation given by Van den Dool and Kratz (1963), linear temperature programmed retention indices (LTPRI) values were calculated on the basis of the chromatograms of samples as well as the chromatograms recorded for the mixture of C₈–C₄₀ *n*-alkanes. Next, the LTPRI values were compared to indexes available in catalogs (de Zeeuw et al. 1992; Sadtler Research Laboratory 1986; Adams 1995; NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>) and in our previous publication (Isidorov et al. 2005a, b). The names of all compounds fully identified are shown in Table 1 with no additional marks. It means that mass spectral data matched library spectra, and GC retention index data matched library index. The compounds tentatively identified, marked with (a), refer to identities whose spectral data matched those found in the library; however, their retention index values could not be found in the literature, or their determination was not possible.

All identified compounds were categorized into the following groups: aliphatic hydrocarbons, aromatic hydrocarbons, terpenes, sulfur compounds, ethers, alcohols, chloride compounds, esters, carbonyls, nitrogen-containing compounds, and non-identified compounds. In the course of laboratory research, 164 organic compounds of various structures were registered. The substances in largest amounts found in the laboratory research included ethyl ether, *n*-hexane, *o,p*-xylene, mesitylene, *m*-ethylbenzene, limonene, *n*-decane, *n*-undecane, and *n*-dodecane. The most numerous group of compounds were aliphatic and aromatic hydrocarbons. In the group of aliphatic hydrocarbons, compounds of saturated character and linear structure (*n*-alkanes C₈ – C₃₃) and branched compounds (methylnonane, methyldecane, methylundecane, etc.) were predominating. The relative percentage (calculated as a fraction of the total ion current, TIC quotient between the sum of peak areas of compounds belonging to a particular group and the sum of peak areas of all

Table 1 Identification results of organic compounds emitted from municipal sludges and values of parameters used in identification process

Compound	CAS#	<i>LTPRI</i> ^{Exp}	<i>LTPRI</i> ^{Lit}	<i>m/z</i>	<i>M</i> ^{•+}	Occurrence
Methyl alcohol ^a	67–56–1	–	381	31, 29(73), 30	32	w, y, z
Methanethiol ^a	74–93–1	–	–	47, 48(80), 45(51), 46	48	w, x, y
Ethanol ^a	64–17–5	–	448	31, 45(75), 27(46), 46, 55	46	w, x, z
Acetone ^b	67–64–1	500	500	43, 58(37), 41(11), 42, 39	58	w, x, y, z
Trimethylamine ^a	75–50–3	–	503	58, 59(50), 42(34), 43	59	z
Ethyl ether	60–29–7	510	509	31, 59(88), 74(70), 45, 29	74	w, x, y, z
Dimethyl sulfide	75–18–3	521	514	62, 47(75), 45(45), 46, 61	62	w, y
Methylene chloride ^{b,c}	75–09–2	531	528	86, 84(73), 49(65), 51, 29	84	w
Carbon disulfide ^b	75–15–0	536	540	76, 78(9), 44(9), 38	76	w, x, y, z
<i>n</i> -Hexane	110–54–3	600	600	57, 41(66), 43(56), 56, 42	86	w, x, y, z
2-Butanone ^b	78–93–3	602	602	43, 72(32), 29(15), 57, 27	72	y
Ethene, 1,2-dichloro-, (<i>Z</i>) ^{a,b,c}	156–59–2	608	–	96, 61(91), 98(64), 63, 60	96	w
Ethyl acetate	141–78–6	612	607	43, 61(21), 70(17), 45, 29	88	w, x, y, z
Trichloromethane ^{b,c}	67–66–3	615	616	83, 85(62), 47(16), 87, 48	118	w
Benzene ^{b,c}	71–43–2	653	657	78, 77(23), 51(12), 52, 50	78	w, x, y
3-Pentanone	96–22–0	689	688	43, 41(25), 86(20)	86	w
<i>n</i> -Heptane	142–82–5	700	700	43, 28(60), 41(59), 57, 71	100	w, x
Trichloroethylene ^{b,c}	79–01–6	701	702	132, 95(85), 130	130	w
Bromodichloromethane ^{b,c}	75–27–4	706	709	83, 85(66)	–	w
Furan, 2,5-dimethyl-	625–86–5	706	712	96, 95(80), 43(39), 53, 81	96	w
Disulfide, dimethyl	624–92–0	735	733	94, 79(40), 45, 40	94	w, y, z
Pyridine	110–86–1	736	753	79, 52(47), 51(24), 50, 78	79	w, x, z
Toluene ^{b,c}	108–88–3	757	760	91, 92(64), 65(10), 39, 93	92	w, x, y, z
Thiophene, 3-methyl-	616–44–4	784	786	97, 98(54), 45, 51	98	w
3-Pentanone, 2,4-dimethyl-	565–80–0	794	794	43, 71(46), 41(28),	114	w
<i>n</i> -Octane	111–65–9	800	800	43, 85(84), 41(82), 57, 71	114	w, x
Tetrachloroethylene ^{b,c}	127–18–4	806	814	166, 164(82), 129(69), 131, 168	164	w
Ethylbenzene ^{b,c}	100–41–4	857	850	91, 106(38), 92, 77	106	w, x, y, z
<i>p</i> -Xylene ^b	106–42–3	865	862	91, 106(59), 105(27), 77, 51	106	w, x, y, z
<i>o</i> -Xylene ^b	95–47–6	889	879	91, 106(54), 105(21), 77, 92	106	w, x, y, z
<i>n</i> -Nonane	111–84–2	900	900	43, 57(94), 41(52), 85, 71	128	w
Benzene, 1-methylethyl-	98–82–8	922	914	105, 120(28), 77(20), 103	120	w
α -Thujene	2867–05–2	929	928	93, 91(49), 79, 51	136	x
<i>p</i> -Menthene, trans- ^a	1124–25–0	945	–	81, 68(96), 95, 91	138	w
Benzene, propyl-	103–65–1	950	944	91, 120(28), 92(12), 65, 78	120	w, x, y, z
Benzene, 1-ethyl-3-methyl	620–14–4	958	960	105, 120(35), 91(10), 77, 106	120	w, x, y, z
Nonane, 5-methyl-	15869–85–9	959	961	43, 85(71), 53(46), 84, 29	142	w
Benzene, 1-ethyl-4-methyl-	622–96–8	960	963	105, 120(33), 91(10), 77, 106	120	w, x, y
Nonane, 4-methyl-	52896–95–4	961	963	57, 43(66), 28(50), 70, 71	142	w
Dimethyl trisulfide	3658–80–8	962	976	126, 79(41), 128(32), 64, 111	126	w, x, y, z
Aliphatic-aromatic hydrocarbon	–	965	–	105, 120(57), 119(15), 77, 91	120	w, x
Benzene, 1-ethyl-4-methyl-	622–96–8	966	963	105, 120(56), 77(13), 91, 119	120	z
1-Heptanol	111–70–6	969	970	70, 55(83), 69, 41	–	w
Nonane, 3-methyl-	5911–04–6	970	972	57, 71(72), 41(61), 93, 43	–	w
Sabinene	3387–41–5	971	976	93, 91(50), 79(49), 69	136	x
4-Octanone	589–63–9	975	970	71, 85(77), 57(57), 43, 41	128	x
Benzene, 1-ethyl-2-methyl-	611–14–3	976	976	105, 120(34), 91(10), 77, 106	120	w, x, y, z
<i>p</i> -Menthane, trans-	1678–82–6	979	978	97, 55(81), 41(40), 207, 69	140	w
Benzene, 1,3,5-trimethyl-	108–67–8	989	994	105, 120(52), 119(13), 77, 91	120	w, x, y, z
Phenol ^c	108–95–2	994	982	94, 66(26), 65(21), 39, 95	94	w, x, y, z

Table 1 (continued)

Compound	CAS#	<i>LTPRI</i> ^{Exp}	<i>LTPRI</i> ^{Lit}	<i>m/z</i>	<i>M</i> ^{•+}	Occurrence
<i>n</i> -Decane	124–18–5	1000	1000	57, 43(76), 71(45), 105, 41	142	w, x, y, z
Benzene, 2-methylpropyl-	538–93–2	1003	1009	91, 92, 134	134	x
α -Phellandrene	99–83–2	1005	1005	93, 77(51), 92(48), 85, 69	136	w
3-Carene	13466–78–9	1006	1010	93, 91(40), 105(37), 79, 77	136	w, x
Benzene, 1,3-dichloro- ^{b,c}	541–73–1	1007	1011	146, 148(96), 111(67), 50, 281	146	w
Benzene, 1,2,3-trimethyl-	526–73–8	1017	1020	105, 120(48), 119(13), 77, 106	120	w, x, y, z
Benzene, (1-methylethyl)-1-methyl-4-	99–87–6	1020	1020	119, 134(34), 91(16), 117	134	w, x, y, z
Benzene, (1-methylethyl)-1-methyl-2-	527–84–4	1022	1022	119, 134(29), 91(18), 117, 120	134	w
Nonane, 2,6-dimethyl-	17302–28–2	1022	1030	71, 43(71), 57(68), 70, 41	–	w, x, y, z
Limonene	138–86–3	1025	1031	68, 93(85), 67(76), 79, 94	136	w, x, y
Cyclohexane, butyl-	1678–93–9	1027	1025	83, 82(74), 55(68), 105, 41	140	w, x, y
Indane	496–11–7	1029	1034	117, 118(53), 115(30), 119, 91	118	w, x, y, z
Cyclopentane, pentyl-	3741–00–2	1033	1032	69, 68(79), 41(63), 55, 70	140	w, x
Naphthalene, decahydro-, trans-	493–02–7	1046	1057	138, 67(73), 82(59), 95, 81	138	w, x, y, z
Benzene, 1,3-diethyl-	141–93–5	1047	1035	119, 105(99), 134(48), 91, 103	134	w, x, z
Benzene, 1-methyl-4-propyl-	1074–55–1	1048	1038	105, 134(18), 79(11), 106, 77	134	w, x, z
Benzene, 1-methyl-3-propyl-	1074–43–7	1049	1055	105, 134(29), 106(14), 91, 77	134	w, x, y, z
Benzene, 1,2-diethyl-	135–01–3	1052	1057	105, 134(29), 28(20), 119, 91	134	w, x
Benzene, butyl-	104–51–8	1053	1054	91, 92(68), 134(49), 119, 41	134	w, x, y, z
Benzene, 1-ethyl-1,3-dimethyl-	934–74–7	1056	1055	119, 134(38), 91(14), 105, 120	134	w, x, y, z
Decane, 5-methyl-	13151–35–4	1058	1058	57, 43(57), 85(39), 119, 41	–	w, x, y
Decane, 4-methyl-	2847–72–5	1061	1060	71, 57(63), 43(54), 70, 41	–	w, x, y, z
Benzene, 1-methyl-2-propyl-	1074–17–5	1063	1063	105, 134(25), 77(11), 106, 79	134	w, x, y, z
Decane, 2-methyl-	6975–98–0	1065	1064	57, 43(89), 71(77), 85, 41	–	w, x, y, z
Decane, 3-methyl-	13151–34–3	1071	1072	71, 57(98), 85(62), 43, 41	–	w, x, y, z
Benzene, 2-ethyl-1,4-dimethyl-	1758–88–9	1074	1072	119, 134(35), 91(14), 117, 115	134	w, x, y, z
Benzene, 1-ethyl-2,4-dimethyl-	874–41–9	1075	1075	119, 134(33), 117(14), 91, 120	134	w, x, y, z
Aliphatic cyclohexane derivative	–	1080	–	97, 55(45), 96(38), 154, 117	–	w
Benzene, 4-ethyl-1,2-dimethyl-	934–80–5	1082	1088	119, 134(30), 91(13), 120, 41	134	z
Benzene, 1,2,3,4-tetramethyl-	488–23–3	1082	1078	119, 134(35), 91(14), 120, 117	134	w, x, y
Phenol, 3-methyl-	108–39–4	1083	1075	108, 108(94), 79(17), 77, 53	108	y, z
Fenchone	1195–79–5	1084	1089	81, 69(47), 41	152	x
Isoterpinolene	586–63–0	1085	1086	136, 91(99), 41(67), 111, 83	136	x
NN	–	1085	–	69, 111(92), 121(68), 79, 125	–	w
Naphthalene, decahydro-, cis-	493–01–6	1089	1097	81, 96(96), 138(79), 67, 82	138	x
<i>n</i> -Undecane	1120–21–4	1100	1100	57, 43(73), 71(59), 85, 41	156	w, x, y, z
Benzene, 1-ethyl-2,3-dimethyl-	933–98–2	1106	1104	134, 119(97), 81(73), 207, 77	134	w, y
1,3,8- <i>p</i> -Menthatriene	21195–59–5	1111	1111	119, 134(53), 117(15), 91, 115	134	w, x, y, z
Benzene, 1,2,4,5-tetramethyl-	95–93–2	1115	1123	119, 134(51), 91(11), 115, 120	134	w, x, y, z
Naphthalene, decahydro- α -methyl-, trans- ^a	2547–27–5	1117	–	152, 82(86), 95(84), 84, 127	152	w, x, y, z
Decane, 2,6-dimethyl-	13150–81–7	1121	1119	57, 71(79), 119(59), 112, 109	170	w
Branched alkane	–	1123	–	71, 57(87), 70(62), 43, 56	–	w
Decane, 3,7-dimethyl-	17312–54–8	1127	1125	71, 57(99), 85(84), 43, 70	–	w, x, y, z
Cyclohexane, pentyl-	4292–92–6	1130	1130	83, 82(75), 55(62), 69, 41	154	w, x, y, z
Decane, 3,8-dimethyl-	17312–55–9	1133	1140	57, 71(71), 43(46), 85, 41	–	y
Cyclopentane, hexyl-	4457–00–5	1136	1134	69, 41(99), 68(94), 83, 84	154	w, y, z
Cyclohexanone, 2-propyl-	94–65–5	1136	1134	98, 55(25), 32, 41	140	x, z

Table 1 (continued)

Compound	CAS#	<i>LTPRI</i> ^{Exp}	<i>LTPRI</i> ^{Lit}	<i>m/z</i>	<i>M</i> ^{•+}	Occurrence
Naphthalene, decahydro-2-methyl-	2958–76–1	1140	1138	57, 95(83), 85(80), 111, 152	152	w, x, y
Benzene, 1,2,3,5-tetramethyl-	527–53–7	1147	1145	119, 134(61), 41(43), 81, 91	134	w, x, y
<i>p</i> -Menthone	89–80–5	1150	1154	112, 71(73), 73(68), 69, 105	154	w, x, z
Undecane, 6-methyl-	17302–33–9	1155	1154	57, 98(35), 43(22), 41, 56	–	w, x, y
Naphthalene, 1,2,3, 4-tetrahydro-	119–64–2	1155	1158	104, 98(91), 57(70), 132, 58	132	w
Undecane, 5-methyl-	1632–70–8	1156	1156	71, 43(98), 85(68), 84, 112	–	w, x, y, z
Undecane, 4-methyl-	2980–69–0	1160	1160	71, 43(74), 85(48), 57, 70	–	w, x, y, z
Undecane, 2-methyl-	7045–71–8	1167	1164	43, 57(98), 71(81), 85, 41	–	w
Undecane, 3-methyl-	1002–43–3	1171	1171	57, 85(64), 71(62), 43, 41	–	w, x, y, z
Menthol	89–78–1	1170	1173	71, 57(57), 41(49), 43, 86	–	y, z
Naphthalene ^c	91–20–3	1176	1179	128, 127(16), 28(12), 95, 129	128	w, x, y, z
Cyclohexane derivative	–	1182	–	97, 55(53), 131(20), 96	–	w, x, y
NN	–	1186	–	69, 83(96), 91(89), 168, 111	–	w, x, y
NN	–	1196	–	97, 133(68), 96(66), 95	–	w, x
<i>n</i> -Dodecane	112–40–3	1200	1200	57, 43(73), 71(64), 85, 41	170	w, x
Undecane, 2,6-dimethyl-	17301–23–4	1214	1216	57, 71(48), 43(34), 41, 56	184	w, x, y, z
Naphthalene, 2-ethyldecahydro-	66660–40–0	1216	–	81, 137(83), 95(78), 97, 109	166	w, x, y, z
Undecane, 3,7-dimethyl-	17301–29–0	1221	1222	43, 57(98), 85(79), 71, 41	–	w, x
Cyclohexane, hexyl-	4292–75–5	1234	1233	83, 82(84), 55(57), 67, 41	168	w, x, y, z
Caprolactam ^a	105–60–2	1244	–	55, 113(64), 84, 85	113	x
Dodecane, 6-methyl-	6044–71–9	1253	1253	57, 71(67), 43(43), 41, 29	–	w, x, y
Dodecane, 5-methyl-	17453–93–9	1255	1255	43, 85(89), 84(68), 83, 97	–	w, x, y
Dodecane, 4-methyl-	6117–97–1	1259	1260	71, 43(72), 85(65), 70, 57	–	w, x, y
Dodecane, 2-methyl-	1560–97–0	1263	1265	57, 43(82), 85(62), 70, 71	–	w, x, y
Dodecane, 3-methyl-	17312–57–1	1270	1271	57, 85(55), 43, 71	–	w
Decane, 1-chloro-	1002–69–3	1264	1261	43, 85(88), 57(88), 71, 69	–	w, y
Dodecane, 3-methyl-	17312–57–1	1273	1271	71, 57(99), 43(45), 113, 112	–	w, x, y
Naphthalene, 2-methyl-	91–57–6	1286	1291	141, 142(85), 71(47), 115, 83	142	w, x, y, z
Indole	120–72–9	1294	1292	117, 90(38), 89(26), 118, 116	117	y, z
<i>n</i> -Tridecane	629–50–5	1300	1300	57, 43(77), 71(72), 85, 41	184	w, x, y, z
Naphthalene, 1-methyl-	90–12–0	1301	1308	142, 141(85), 115, 117	142	x, z
Naphthalene, 1,2,3, 4-tetrahydro-2,7-dimethyl-	13065–07–1	1311	1302	160, 117(49), 118, 71	160	x, z
Phthalic anhydride	85–44–9	1313	1319	104, 76(57), 50(25), 74, 148	148	w
Nonane, 2,2,4,4,6,8, 8-heptamethyl-	4390–04–9	1317	1323	57, 41(18), 85(18), 71, 99	–	w, x
Tridecane, 7-methyl-	26730–14–3	1351	1351	57, 71(81), 159(50), 105	–	x
Tridecane, 4-methyl-	26730–12–1	1359	1360	57, 71(88), 43(66), 85	–	x
Tridecane, 2-methyl-	1560–96–9	1363	1365	85, 57(71), 71(67), 97, 43	–	x
Tridecane, 3-methyl-	6418–41–3	1370	1371	57, 71(62), 28(50), 43, 41	–	x, z
Copaene	3856–25–5	1370	1376	105, 119(97), 161(63), 81, 77	204	y
Dodecane, 2,6,10-trimethyl-	3891–98–3	1376	1382	57, 71(88), 85(56), 41, 43	–	w, x
Diphenyl ether ^a	101–84–8	1396	–	170, 141(62), 142(30), 77, 168	170	x, y, z
β -Elemene	515–13–9	1397	1391	189, 93(92), 161(85), 65, 137	204	w
<i>n</i> -Tetradecane	629–59–4	1400	1400	57, 43(62), 71(59), 85, 41	198	w, x, y, z
(<i>E</i>)- β -Caryophyllene	87–44–5	1413	1419	91, 133(93), 93(93), 79	204	w, x, y
Branched alkane	–	1417	–	57, 71(91), 85(72), 43, 70	–	w, x, z
Branched alkane	–	1423	–	57, 71(71), 97(69), 55, 56	–	w, x, y, z
Branched alkane	–	1439	–	57, 71(86), 113(46), 43, 85	–	w, x, y, z
Branched alkane	–	1441	–	57, 71(72), 43(55), 112, 197	–	w, x, z

Table 1 (continued)

Compound	CAS#	<i>LTPRI</i> ^{Exp}	<i>LTPRI</i> ^{Lit}	<i>m/z</i>	<i>M</i> ^{•+}	Occurrence
α -Humulene	6753-98-6	1448	1453	93, 71(46), 57(40), 80	204	w, x, y
Tetradecane, 5-methyl-	25117-24-2	1454	1454	57, 85(76), 169	212	w, x, y
Tetradecane, 2-methyl-	1560-95-8	1461	1465	57, 85(78), 97(56), 55, 83	212	w, x, y
Tetradecane, 3-methyl-	18435-22-8	1468	1472	57, 71(79), 85(62), 113, 70	—	w
Acenaphthene	83-32-9	1472	1476	154, 153(98), 125, 70	154	x, z
Branched alkane	—	1477	—	71, 57(92), 43(61), 113, 70	—	w, x, y, z
<i>n</i> -Pentadecane	629-62-9	1499	1500	57, 71(77), 85(59), 43, 41	212	w, x, y, z
Butylated hydroxytoluene	128-37-0	1511	1512	205, 220(27), 206(180), 145, 177	220	w, x, y
Calamene	483-77-2	1519	1523	159, 160(15), 128(13), 202, 43	202	y
Benzene, 1-butylhexyl- ^a	4537-11-05	1535	—	91, 147(31), 161(20), 104, 29	218	w, z
Benzene, 1,3,5-tri-tert-butyl- ^a	1460-02-2	1555	—	231, 246(28), 216(24), 232, 215	246	w
Pentadecane, 2-methyl-	1560-93-6	1569	1564	57, 71(59), 43, 55	226	z
Diethyl phthalate ^c	84-66-2	1594	1591	149, 177(23), 32, 28	—	w
<i>n</i> -Hexadecane	544-76-3	1599	1600	57, 71(61), 85(50), 43, 55	226	w, x, z
Benzophenone ^c	119-61-9	1623	1640	105, 182(48), 77	182	w, x
Benzene, 1-butylheptyl-	4537-15-9	1633	1628	91, 44(43), 105(37), 147,	232	w, z
Benzene, 1-propyloctyl-	4536-86-1	1643	1638	91, 92(41), 43, 189	232	w
Naphthalene, 1,	483-78-3	1671	1674	183, 198(63)	198	w
6-dimethyl-4-(1-methylethyl)-						
Benzene, 1-pentylheptyl-	2719-62-2	1727	1725	91, 105(27), 191, 39	246	z
Benzene, 1-butyloctyl-	2719-63-3	1731	1729	91, 71(46), 85(32), 57, 69	246	z
Isopropyl myristate	110-27-0	1818	1827	43, 228(72), 57(67), 102, 41	—	w
Dibutyl phthalate ^c	84-74-2	1960	1954	149, 150(11), 223(6), 104, 41	—	w, y
Cyclic octaatomic sulfur	10544-50-0	1998	2004	64, 256(59), 160(48), 192, 128	256	x, z
Diisooctyl phthalate ^c	27554-26-3	2545	2540	149, 167(33), 57(16), 279, 150	—	w, x
<i>n</i> -Heptacosane	593-49-7	2699	2700	57, 71(81), 43(64), 85, 41	380	x
<i>n</i> -Octacosane	630-02-4	2803	2800	57, 71(72), 43(69), 85, 55	394	x
<i>n</i> -Nonacosane	630-03-5	2903	2900	57, 71(83), 43(56), 85, 55	408	x
<i>n</i> -Triacontane	638-68-6	2999	3000	57, 71(82), 85(64), 43, 55	422	x
<i>n</i> -Hentriacontane	630-04-6	3100	3100	57, 71(75), 43(52), 85, 97	436	x
<i>n</i> -Dotriacontane	544-85-4	3198	3200	57, 71(67), 43(56), 85, 55	450	x
<i>n</i> -Tritriacontane	630-05-7	3302	3300	57, 43(91), 71(82), 85	462	x

LTPRI^{Exp} linear temperature programmed retention index determined in the course of research, *LTPRI*^{Lit} retention index found in the literature, *m/z* mass/charge ratio values of main and most intensive peaks of the mass spectrum (intensities are given in parenthesis), *M*^{•+} mass of the molecular ion, *w* laboratory investigation with CAR/PDMS fiber coating, *x* laboratory investigation with DVB/CAR/PDMS fiber coating, *y* field investigation with CAR/PDMS fiber coating, *z* field investigation with DVB/CAR/PDMS fiber coating

^aTentatively identified compounds

^bCompounds included in EPA list of target compounds

^cCompounds included in EPA list of priority pollutants

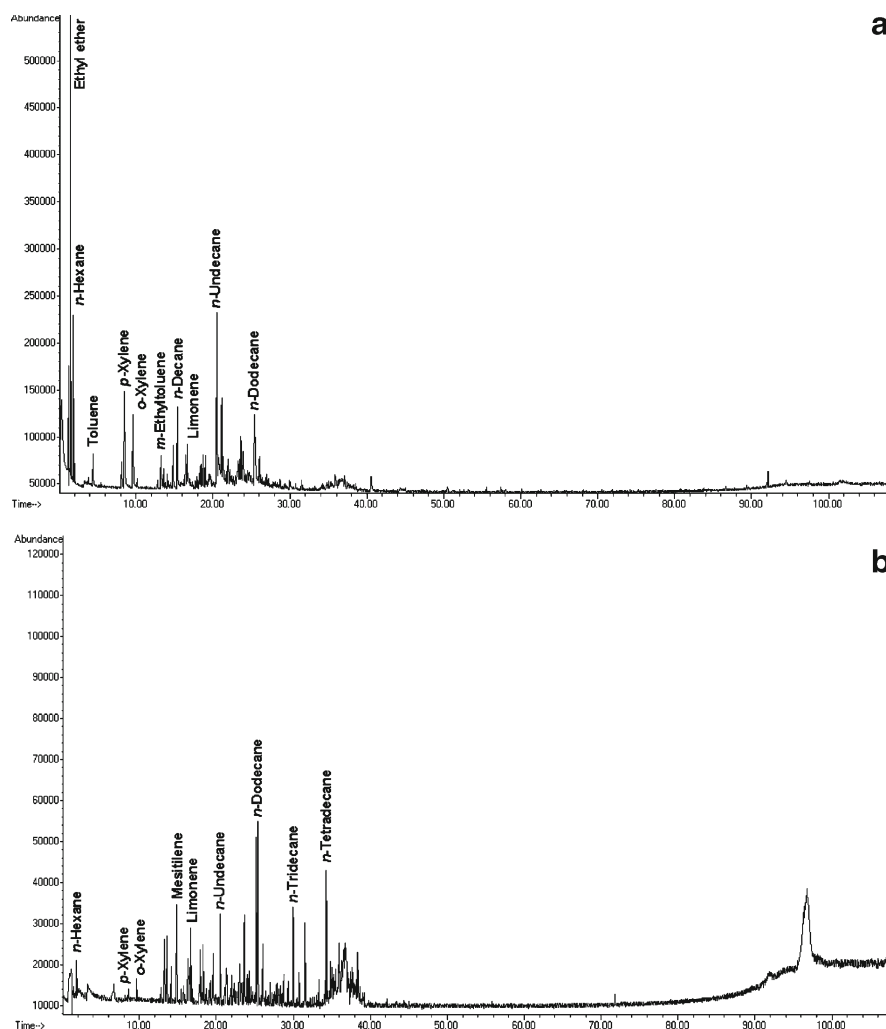
detected compounds) of aliphatic hydrocarbons ranged between 21% and 83% of TIC in the course of research carried out in various variants and on various dates.

Both monocyclic compounds—benzene, toluene, xylenes, and others, as well as naphthalene and its derivatives were found in the group of aromatic hydrocarbons, which constituted between 8% and 48% of TIC, whereas terpenes made from 1% to over 13% of total VOCs and SVOCs

emission through sludge. The content of other groups of compounds lay within the range from less than 1% to 10% of TIC depending on the variant and time of determination. Substances containing sulfur included such compounds as carbon disulfide, dimethyl sulfide, dimethyl disulfide, and cyclic octaatomic sulfur. Among others, in the group of carbonyl compounds, the following were identified: acetone, 3-pentanone, 4-octanone, whereas esters included ethyl acetates

Fig. 1 The chromatograms obtained during HS-SPME/GC–MS analysis of sewage samples:

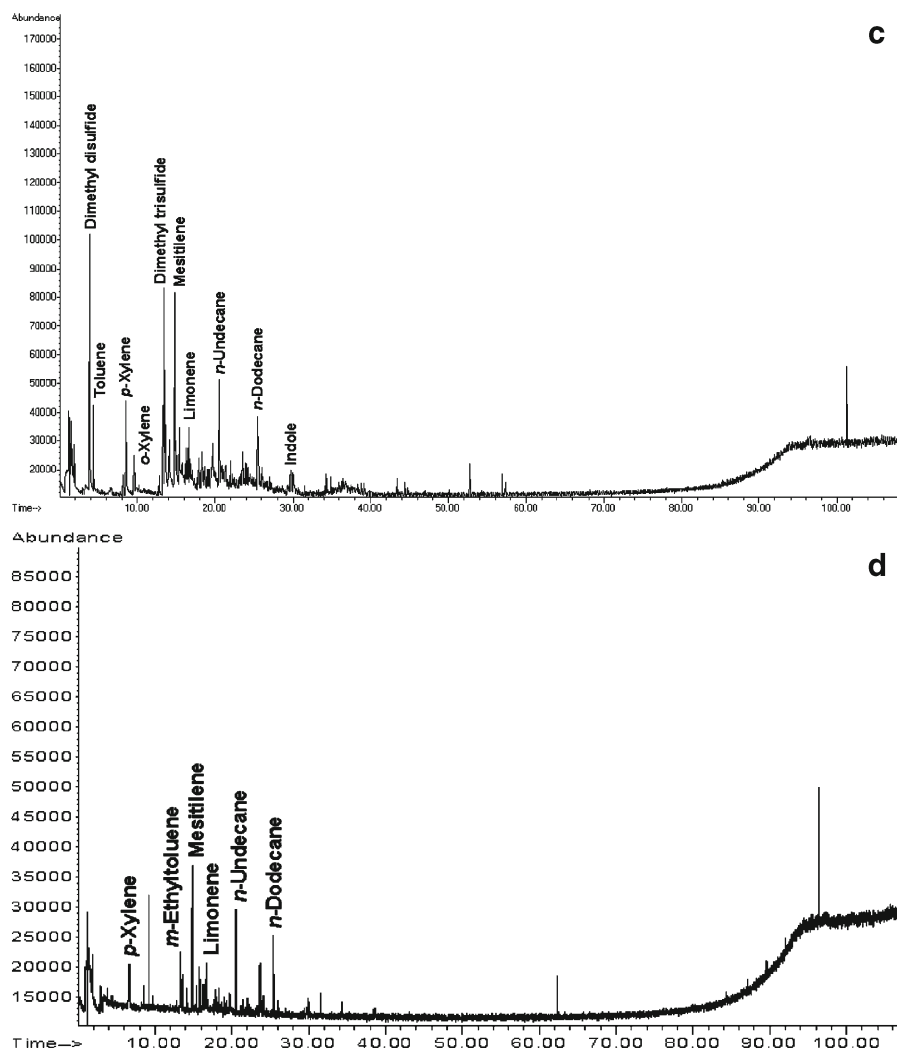
a laboratory investigation with CAR/PDMS fiber coating;
b laboratory investigation with DVB/CAR/PDMS fiber coating;
c field investigation with CAR/PDMS fiber coating;
d field investigation with DVB/CAR/PDMS fiber coating



and phthalic acids. Main chlorine compounds determined in the sewage sludge were: methylene chloride, 1,2-dichloroethene, trichloroethylene, bromodichloromethane, and tetrachloroethylene. Percentages of individual groups of compounds identified in the laboratory analysis using SPME fibers with different coatings are shown in Fig. 2.

Detected and identified were also about 100 organic compounds emitted from the sewage sludge stored on the heap. A few compounds identified in the course of extraction carried out on the heap, including: triethylamine, 2-butanone, 1-ethyl-4-methylbenzene, 4-ethyl-1,2-dimethylbenzene, 3-methylphenol, menthol, indole, copaene, calamene, 2-methylpentadecane, 1-pentylheptyl-

benzene, and 1-butyloctylbenzene were not recorded during laboratory determinations. Among compounds extracted directly on the sludge heap, the following compounds were characterized with greatest intensity: dimethyl disulfide, dimethyl trisulfide, mesitylene, toluene, *p*-xylene, *o*-xylene, limonene, *n*-decane, *n*-undecane, indoles, and ethylbenzene. Similarly, as during laboratory research, the largest group made aliphatic hydrocarbons of linear, branched, and cyclical structure (27% to 58% of total VOC emission) and aromatic hydrocarbons, i.e., benzene, naphthalene, and their derivatives (14% to 55%). Significant portion (5% to over 25%) of VOC emission through the sludge heap makes sulfur compounds, what is a substantial increase in comparison with

Fig. 1 (continued)

the results of laboratory research. During research on the heap were also detected: terpenes (2.5% to 5%, main compounds: limonene, menthone), nitrogen compounds (from almost 1% to 8%, e.g., indole, trimethylamine), as well as ketones, alcohols, ethers, esters, and chlorine compounds, whose content varied within the range from 0% to 4%. Percentage of individual groups of compounds determined in field analysis is provided in Fig. 3.

Volatile and semi-volatile organic compounds detected in the sewage sludge can be divided into two groups: compounds of natural origin and synthetic substances. The majority of compounds extracted from the sewage sludge composed of natural compounds derived from human excre-

ments, nutritional remains, and products of their decomposition. Among VOCs detected in the sludge substances of natural origin were:

- Simple and branched alkanes, e.g., decane, undecane, contained in plant waxes;
- Terpenes and terpenoids, e.g., phellandrene, 3-carene, derived from plant tissues;
- Substances of final products of various organic metabolic processes, including organisms forming active sludge, e.g., sulfane, carbon disulfide, dimethyl polysulfides, methanol, ethanol.

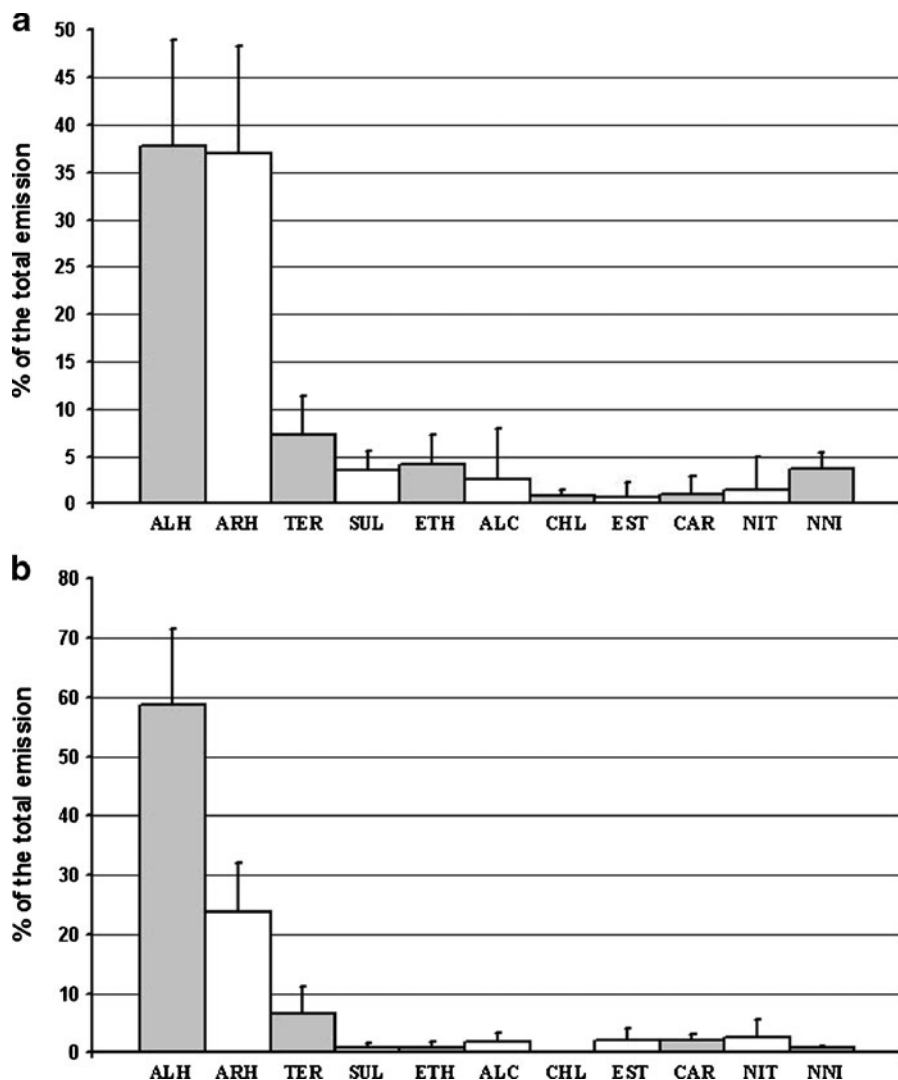
Synthetic substances present in the sewage sludge are less susceptible to biodegradation than natural compounds; thus, they can accumulate in

Fig. 2 The percentage of individual group of compounds obtained in laboratory analysis with different fiber coatings.

a CAR/PDMS;

b DVB/CAR/PDMS.

ALH aliphatic hydrocarbons, *ARH* aromatic hydrocarbons, *TER* terpenes, *SUL* sulfur compounds, *ETH* ethers, *ALC* alcohols, *CHL* chloride compounds, *EST* esters, *CAR* carbonyls, *NIT* nitrogen compounds, *NNI* nonidentified compounds



the sludge and—eventually—in the natural environment. Synthetic substances emitted from the sewage included:

- Alkylbenzenes, e.g., mesitylene, xylenes—components of solvents, synthetic oils, greases, bitumen masses;
- Chlorine-containing substances: chloroform and methylene chloride—popular organic solvents, benzene chloride—intermediate product of pharmaceutical industry and component of dyestuffs, bromodichloromethane, and dichloroethenes—by-products of water disinfection;
- Remains of hygiene articles used in the household: limonene and menthol—aromatizing agents for washing-up liquids and toothpastes;
- Plasticizers—diethyl phthalate, diisooctyl phthalate, dibutyl phthalate, phthalic anhydride;
- Butylated hydroxytoluene—popular antioxidant added to food, cosmetics, drugs, rubber, etc.;
- Benzophenone—sunscreen agent;
- PAH, e.g., naphthalene—used as an intermediate product in the production of dyestuffs, dissolvents, synthetic resins, and insecticides.

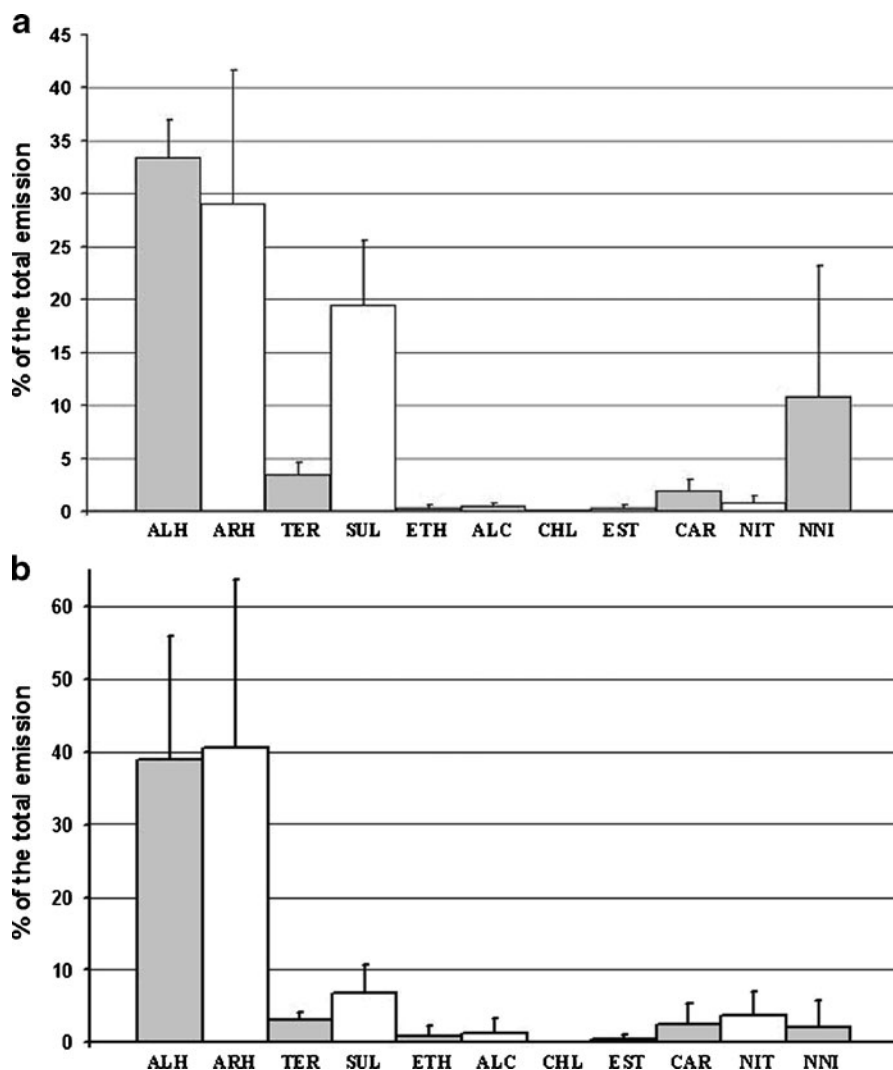
Some substances detected in the sludge are known for their harmful influence on human

Fig. 3 The percentage of individual group of compounds obtained in field analysis with different fiber coatings.

a CAR/PDMS;

b DVB/CAR/PDMS.

ALH aliphatic hydrocarbons, *ARH* aromatic hydrocarbons, *TER* terpenes, *SUL* sulfur compounds, *ETH* ethers, *ALC* alcohols, *CHL* chloride compounds, *EST* esters, *CAR* carbonyls, *NIT* nitrogen compounds, *NNI* nonidentified compounds



health and natural environment. Sixteen compounds (marked with superscripted “c” in Table 1) detected in the sludge are included on the list of priority pollutants established by EPA, and other 16 chemicals (marked with superscripted “b” in Table 1) are on the EPA’s list of target compounds.

Phthalic acid esters are counted as endocrine disrupters and they alter the normal functioning of the endocrine system and cause important reproductive and developmental alterations, such as feminization and decreased fertility (Arcadi et al. 1998). Naphthalene is defined by the US Environmental Protection Agency as hazardous to environment. Exposition to high concentration

of naphthalene can damage or destroy red blood cells and cause hemolytic anemia, (Lu et al. 2005). Carbon disulfide has been classified in the US as a hazardous air pollutant in Title III of the Clean Air Act Amendments of 1990. Hydrogen sulfide is subjected to a stringent control for its environmental release due to its toxicity, unpleasant odor, and corrosive properties (Janssen et al. 1997). Benzene, toluene, ethyl benzene, and xylenes are known carcinogens and pose a risk to both human health as well as other forms of life (Fang et al. 2004). The activity of butylated hydroxytoluene has been found to be ambiguous as its toxicological allegations are still being questioned. Thus, in some studies, cancer growth related to its

activity was shown to be increasing but decreasing in others (Tryphonas et al. 1999; Safer and al-Nughamish 1999; Parke and Lewis 1992).

Conclusions

In the study, the headspace mode of solid-phase micro-extraction to extract volatile and semi-volatile organic compounds from wastewater sludge was used. The HS-SPME technique combined with GC–MS offered a possibility to isolate and detect a wide spectrum of organic pollutants starting from extremely volatile compounds (e.g., methanol, ethanol, acetone) to finish with the compounds of moderate volatility such as phthalic acid esters, hydrocarbons of more than 20 carbon atoms in the molecule. Using the SPME method, the isolation and concentration process of analytes occurs in one stage, and the risk of contamination of the sample by reagents and vessels is considerably reduced. The combination of the two independent parameters: mass spectra and retention indices, allows us to obtain high identification reliability of unknown organic compounds. However, these results are, as yet, preliminary and must be supplemented by precise quantitative analysis. In quantitative analysis, in order to improve SPME extraction results, the use of additional isolation techniques, such as sorbent tubes or traps sampling should be considered.

The presence of substances having harmful influence on human health and natural environment shows the need to monitor such compounds. The monitoring could be especially important in the process of making decisions concerning the methods of municipal sewage sludge management.

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