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SURFACTANTS IN KLODNICA RIVER (KATOWICE, POLAND). PART I. LINEAR ALKYLBENZENE SULPHONATES (LAS)

OBECNOŚĆ ZWIĄZKÓW POWIERZCHNIOWO CZYNNYCH W RZECE KŁODNICA (KATOWICE, POLSKA). CZĘŚĆ I. LINIOWE ALKILOBENZENOSULFONIANY

Abstract: Surfactants are a group of compounds with specific physico-chemical properties and therefore they are used in many spheres of human activity. Surface-active substances undergo various physico-chemical transformations, what enables their migration between different elements of the environment and may lead to its pollution. Selected anionic surfactants were determined in samples of water from the Klodnica river (25 samples) and bottom sediments (25 samples). In most samples the presence of anionic analytes was confirmed. The determined concentration levels were in the range of up to 0.2105 ± 0.0023 mg/dm^3 or 0.207 ± 0.010 µg/kg (surface water and bottom sediment samples, respectively). Comparing the concentrations of certain analytes found in liquid and solid environmental samples, it can be noticed that the surfactants containing a shorter alkyl chain in a molecule were present in higher concentrations in liquid samples (hydrophobicity increasing with the increasing length of the chain) and the other way round.

Keywords: surface-active substances, surface water, industrial area, linear alkylbenzene sulphonates

Introduction

Surfactants, also called surface-active substances, have specific physico-chemical properties, like the ability to lower surface tension and/or interfacial tension between different media as well as to dissolve in solutions of polar and/or non-polar substances [1]. Due to this fact, surface-active substances are used in different aspects of human activity, leading to their (or products of their biodegradation) systematic emission to different

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elements of the environment. Specific properties of surface-active agents lead to their increased mobility and free movement between different elements of the environment [2, 3].

Most of the global production (about 65%) of surface active agents are anionic surfactants [4]. Polar parts of anionic molecules of surfactants contain carboxylic, sulphonic, sulphonate and phosphoric functional groups. Counterions in their molecules include such ions as sodium, potassium, lithium, calcium or protonated amines. Linear alkylbenzene sulphonates (LAS) are chemical compounds used at the largest scale of all anionic surfactants. Their molecules contain a sulphonated aromatic ring attached to an alkyl chain containing from 10 to 16 hydrocarbon groups. Other two groups of surfactants that are the most often used in different areas after LAS compounds include a*lkyl ethoxy sulphates* (AES) and alkyl sulphates (AS) that are produced in the process of sulphonation of ethoxylated alcohols (EA). Molecules of AES compounds contain an alkyl chain built from 11 to up to 17 hydrocarbon groups and up to 8 ethoxylated groups attached to a sulphate functional group. Alkyl sulphate molecules only have an alkyl chain consisting of 12-18 hydrocarbon groups attached to a functional group [4, 5].

The presence of anionic surfactants has been confirmed in samples of atmospheric precipitation and deposits, surface water, bottom sediments, soil and living organisms taken in populated and industrial areas [6-11]. They accumulate in organisms living in aqueous environment and can affect their cell membranes, proteins and enzymes. This phenomenon can lead to impairment of vital functions, cell decay or even death of living organisms. It has also been established that the presence of anionic surfactants leads to lowering surface tension in cells and thus increased susceptibility to absorbing other toxic pollutants by living organisms [12, 13].

Moreover, surface-active substances that are present in aqueous environment are able to form a film on the surface of water, lowering its surface tension. This phenomenon potentially hampers water evaporation and gas transport processes in aqueous ecosystems. The presence of surfactants may lead to increased solubility of other pollutants otherwise poorly soluble in water, what in turn leads to increased mobility of various toxic compounds in aqueous ecosystems [14].

The above mentioned possible impacts of surfactants on the environment prove that it is extremely important to obtain reliable information about the content of anionic surfactants (and products of their breakdown and metabolism) in the water of rivers flowing through industrial areas [2, 3, 15, 16].

In the course of the carried out research environmental samples taken in the Klodnica catchment were used. This catchment is located in a highly urbanised and industrialised area where various pollutants are constantly discharged to aqueous ecosystems as a result of human activity. In the Klodnica catchment surface and underground mining of mineral resources (*e.g.* hard coal) is carried out, what leads to irreversible changes in the hydrographic network of this aqueous ecosystem (land subsidence processes, formation of reservoirs filling the created basins). Moreover, it has been established on the basis of long-term research that the Klodnica is highly polluted throughout *its nearly whole* length due to the emission of various chemical compounds with treated effluents or their discharge without previous treatment. The above aspects confirm the possibility of pollution of the Klodnica's ecosystem with surfactants and comprehensive research in this area is justified [17, 18].

Experimental procedures

Sampling site and sampling method

The carried out research comprised surface water and bottom sediment samples taken in the Klodnica catchment in the period from 2010 to 2013 (liquid samples - four times each year, solid samples - twice in 2012 and 2013). Figure 1 and Table 1 present the location of sampling sites where liquid and solid environmental samples were taken.
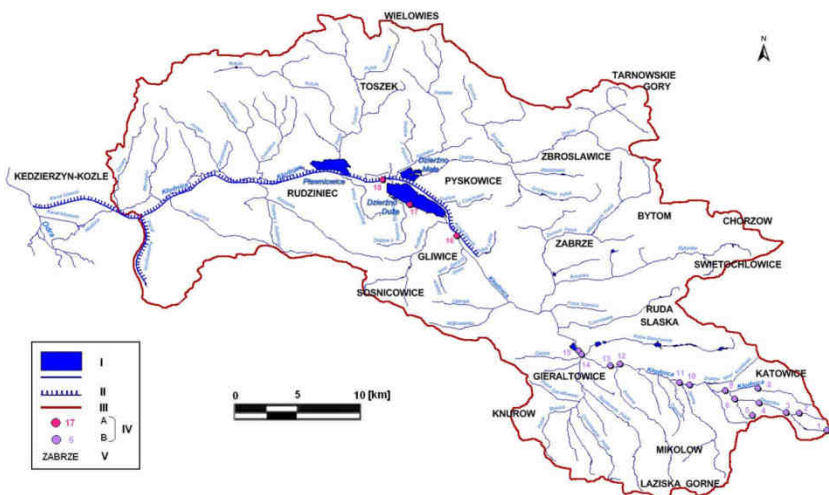
a)
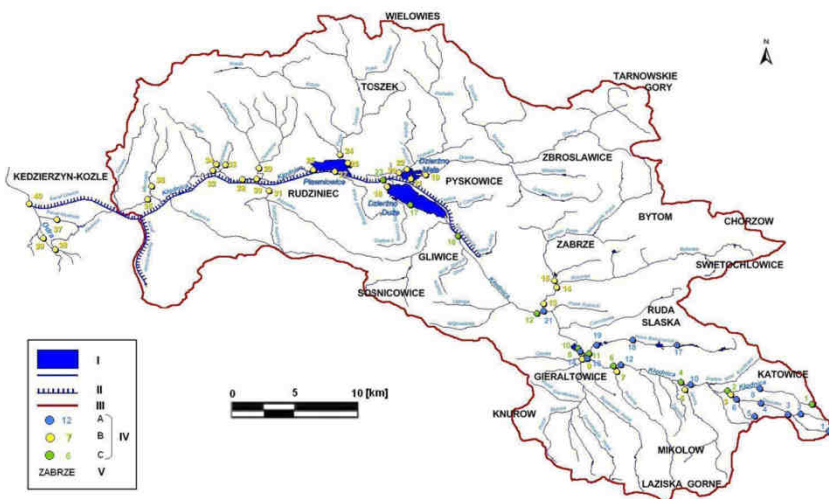
b)

Fig. 1. Surface water (a) and bottom sediment (b) sampling sites. Key: I - watercourses and reservoirs; II - canals; III - borders of the Klodnica catchment; V - cities and a) IV - sampling sites: A - liquid samples taken in 2010-2012, B - liquid samples in 2013, C - samples taken in each campaign; b) IV - sampling sites: A - deposit samples taken in 2012, B - deposit samples taken in 2012 and 2013

Table 1

Information on the samples

Determi-nation of the samples used in a study	Location of environmental samples	GPS coordinates	a) surface water samples taken during the 2010-2012 and 2013		b) samples of bottom sediments collected in 2012 and 2013 years	
			Number of samples taken and number of points			
			Samples 2010-2012 ($n = 23$)	Samples 2013 ($n = 40$)	Samples 2012 ($n = 10$)	Samples 2013 ($n = 15$)
W1	Source of Klodnica	50°13'10.48"N 19°00'37.36"E	7	1	-	-
W/2 O/2	Klodnica - Kokociniec	50°13'96.2"N 18°57'22.3"E	8	-	8	8
W/3 O/3	Source of Slepiotka	50°12'1.60"N 19°02'1.21"E	1	-	1	1
W/4 O/4	The source the 1-st inflow of Slepiotka	50°12'71.6"N 18°59'62.2"E	2	-	2	2
W/5 O/5	Slepiotka - downstream of the confluence of 1-st inflow	50°12'71.5"N 18°59'61.1"E	3	-	3	3
W/6 O/6	Slepiotka - settlement of Zadole	50°13'19.9"N 18°37'65.5"E	4	-	4	4
W/8 O/8	Slepiotka - downstream of the confluence of 2-nd inflow	50°13'43.00"N 18°55'82.4"E	6	-	6	6
W/9 O/9	Downstream of the confluence of the Slepiotka to the Klodnica	50°13'48.93"N 18°54'59.57"E	9	2	9	9
W10	Estuary of the Slepiotka to the Klodnica	50°13'41.73"N 18°55'27.81"E	-	3	-	-
W/11 O/11	Klodnica - above the confluence of Jamna	50°14'01.9"N 18°52'17.6"E	10	-	10	10
W/16 O/16	Downstream of the confluence of the Promna to the Klodnica	50°14'47,47"N 18°47'18,99"E	13	6	13	13
W/17 O/17	Above the confluence of the Potok Bujakowski to the Klodnica	50°15'18,28"N 18°45'30,34"E	14	-	14	14
W/19 O/19	Downstream of the confluence of the Potok Bujakowski to the Klodnica	50°15'18,28"N 18°45'30,34"E	15	8	15	15
W22	Potok Bielszowicki - for KWK Bielszowice	50°16,774'N 18°50,325'E	18	-	-	-
W23	Estuary of the Potok Bielszowicki (Kochlowka) to the Klodnica	50°15'20,08"N 18°45'47,81"E	19	11	-	-
W24	Downstream of the confluence of the Potok Bielszowicki to the Klodnica	50°15'30,02"N 18°45'16,9 5"E	20	10	-	-
W26	Downstream of the confluence of the Bytomka to the Klodnica	50°17'09,23"N 18°42'39,46"E	22	12	-	-
W27	Estuary of the Bytomka to the Klodnica	50°17'24,14"N 18°42'44,27"E	-	13	-	-
W29	Estuary of the Potok Zernicki to the Bytomka	50°19'21,86"N 18°42'254,62"E	-	15	-	-
W/30 O/30	Estuary of the Klodnica to the Dzierzno Duze	50°20'24,93"N 18°37'12,64"E	23	16	-	16
W32	Reservoir of Dzierzno Duze (the western part of reservoir)	50°22'21,28"N 18°32'16,06"E	-	18	-	-
W33	Estuary of the Drama to the Dzierzno Male	50°23'01,39"N 18°34'36,82"E	-	19	-	-

W/36 O/36	Dzierzno Male (the western part of reservoir)	50˚23'19,46''N 18˚33'53,00''E	-	22	-	17
W37	The Gliwice Channel at the estuary of Drama and Klodnica	50˚22'45,47''N 18˚31'37,99''E	25	23	-	-
W/40 O/40	The Lake Plawniowice (the northern part of lake)	50˚23'34,07''N 18˚29'33,96''E	-	26	-	18
W41	The Lake Plawniowice (the southern part of lake)	50˚23'15,86''N 18˚28'25,25''E	-	27	-	-
W42	Downstream of the confluence the Jaryszowka	50˚22'50,95''N 18˚22'59,17''E	-	28	-	-
W44	Downstream of the confluence of the Klodnica to Klodnica	50˚22'41,23''N 18˚23'11,96''E	-	30	-	-
W46	Downstream of the confluence of the Jaroszowiec to the Klodnica	50˚23'11,75''N 18˚20'34,22''E	-	32	-	-
W48	Estuary of the Jordan to the Klodnica	50˚23'16,94''N 18˚20'50,74''E	-	34	-	-
W51	The Klodnica Channel before the confluence to the Odra	50˚20'59,85''N 18˚10'04,12''E	-	37	-	-
W54	The Odra after the estuary to the Klodnica Channel	50˚21'41,25''N 18˚08'09,92''E	-	40	-	-

After collection, liquid samples were transported to the laboratory and stored in reduced temperature until the process of isolation of analytes was carried out with the use of certain analytical techniques (in order to prepare solvent extracts). After collection, samples of bottom sediments were also transported to the laboratory where they were freeze-dried and then stored in a reduced temperature, just like in the case of liquid samples.

Analytical laboratory methods

Table 2 presents basic information concerning selected analytes from the surfactants group, like molar masses, chemical structure and toxicity details of the determined compounds.

Table 2

Basic information concerning properties of selected analytes from the surfactants group

Name/ chemical formula	M [g/mol]	Harmful effects on humans	Toxicity towards animals	References
Sodium linear alkylbenzene sulphonates (LAS) $C_{16-19}H_{25-33}NaO_3S$	320-348	Causes burns of: - eyes - skin	*Daphnia magna* $LC_{50} = 13.9$ mg/dm^3 (48 h) *Dunaliella salina* $EC_{50} = 3.5$ mg/dm^3 (24 h) *Daphnia magna* $LC_{50} = 8.1$ mg/dm^3 (48 h) *Daphnia magna* $LC_{50} = 1.22$ mg/dm^3 (48 h) Mouse: $LD_{50} = 1575$ mg/kg (orally) Rat: $LD_{50} = 404$ mg/kg (orally)	[19-21]

In most cases there are no commercially available suitable standard solutions of the surfactants that are the subject of research, so products with highest available purity were used to prepare basic standard solutions of certain analyte ions with the concentration of 1000 μg/cm^3.

Analytes were dissolved in a small volume of mixture of methanol and deionised water (1:1, v/v) and filled up with enough deionised water to obtain the required volume. Moreover, to limit the process of degradation of analytes, 3 drops of 36% hydrochloric acid were added to the solutions of standard substances.

Then the stock solutions were used to prepare standard mixtures containing certain concentrations of anionic surfactants that were later used at certain stages of analytical procedures. Table 3 contains a breakdown of operating parameters of a chromatographic system during analyses. On the basis of the available literature data, types of fillers of analytical columns and mobile phases used at the stage of separating analytes from the surfactants group were chosen. However, the following parameters were chosen empirically: volume of the dispensed sample, mobile phase flow rate, column temperature or wavelength at the detection stage.

Table 3

Operating conditions of a chromatographic system during identification and quantitative determination of analytes from the anionic surfactants group in environmental samples

| Device type	Ion chromatography system ICS-3000 with autosampler
Analyte type	C_{10}-C_{13} LAS
Volume of dispensed sample [cm^3]	0.005
Eluent composition	A: 100% ACN B: ACN + 100 mM AMAC (pH = 5) (70:30, v:v)
Mobile phase flow rate [cm^3/min]	0.3
Analytical column (Column diameter/length [mm])	Acclaim® Surfactant Plus (2.1/150)
Column temperature [ºC]	30
Detector type	Spectrophotometer detector operating in the UV light range
Wavelength at the detection stage [nm]	225
Time of analysis [min]	20
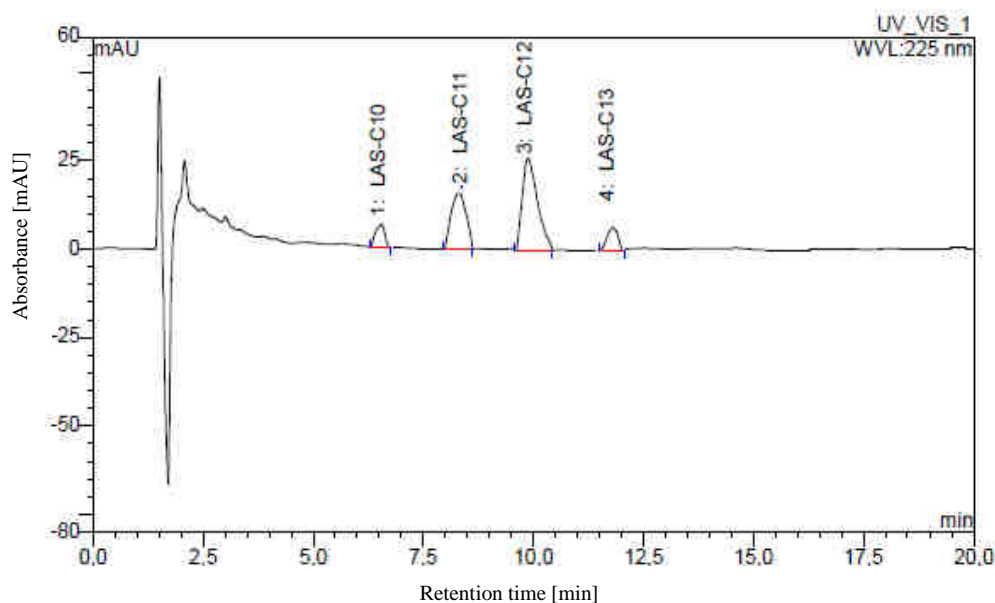
Fig. 2. Chromatogram obtained as a result of chromatographic analysis of a sample of a mixture of standard substances with the concentration of 1-3.3 mg/dm³ with the use of HPIC-UV technique (in optimised conditions)

As a result of analysis chromatograms were obtained presenting the dependence of absorption of radiation of a certain wavelength by molecules of analytes on the time of analysis. A sample chromatogram of a standard solution obtained as a result of chromatography analysis with the use of HPIC-UV system (according to the conditions presented in Table 3) is presented in Figure 2.

In order to make calibration curves a series of water solutions of standard substances was prepared, that contained particular anionic surfactants with concentrations ranging from 5.0 to 3500 µg/dm^3. These solutions were subject to chromatographic analysis in three independent tests. Then calibration curves presenting the dependence of peak area of a certain analyte on its concentration were made. Parameters of calibration curves created with the use of the HPIC-UV system and the calculated values of LOD and LOQ parameters for selected anionic surfactants are presented in Table 4.

Table 4

Parameters of calibration curves for selected anionic surfactants

Analyte	Analyte retention time [min]	Concentration range [µg/dm^3]	Calibration curve equation	Regression coefficient r	LOD [µg/dm^3]	LOQ [µg/dm^3]
C$_{10}$LAS	6.7	LOQ-500	$y = 0.616x + 0.066$	0.9985	4.5	13.5
		500-2500	$y = 1.214x + 0.121$	0.9993		
C$_{11}$LAS	8.4	LOQ-500	$y = 0.331x + 0.137$	0.9997	10.1	30.3
		500-3500	$y = 0.894x + 0.054$	0.9998		
C$_{12}$LAS	9.9	LOQ-500	$y = 0.154x + 0.012$	0.9989	8.4	25.2
		500-3500	$y = 0.851x + 0.109$	0.9991		
C$_{13}$LAS	12.4	LOQ-500	$y = 0.267x + 0.165$	0.9979	11.3	33.9
		500-2500	$y = 0.813x + 0.105$	0.9986		

The calculated values of selected validation parameters of the developed methodologies of determination of selected anionic surfactants in liquid and solid environmental samples are presented in Table 5.

Table 5

Values of selected validation parameters for proposed analytical methodologies determined with the use of ionic chromatography

Analytes	Range of concentrations [µg/dm^3]	Calibration curve equation	Regression coefficient r	LOD [µg/dm^3] or [µg/kg]	LOQ [µg/dm^3] or [µg/kg]	Analyte recovery (CV [%]) ($n = 3$) Repeatability
C$_{10}$-LAS	LOQ-2500	$y = 0.684x + 0.018$	0.9986	8.3	25	89.4 (3.8)
		$y = 0.906x + 0.087*$	0.9985*	12*	36*	88.9 (3.6)*
C$_{11}$-LAS	LOQ-3500	$y = 0.402x + 0.099$	0.9994	11	33	101.2 (2.5)
		$y = 0.427x + 0.133*$	0.9991*	18*	53*	96.4 (3.0)*
C$_{12}$-LAS	LOQ-3500	$y = 0.193x + 0.0588$	0.9995	9.8	29	93.1 (1.4)
		$y = 0.212x + 0.013*$	0.9993*	14*	42*	96.4 (2.8)*
C$_{13}$-LAS	LOQ-2500	$y = 0.298x + 0.112$	0.9997	12	36	97.2 (4.1)
		$y = 0.307x + 0.101*$	0.9992*	19*	54*	96.9 (7.2)*

* selected parameters concern solid samples

Results

Table 6 presents the results obtained at the time of determination of content of analytes from the group of linear alkylbenzene sulphonates in the analysed environmental samples.

Table 6

Content levels of surfactants from the LAS group determined in liquid and solid environmental samples with the use of the developed analytical procedures

Sample determination	C$_{10}$-LAS	C$_{11}$-LAS	C$_{12}$-LAS	C$_{13}$-LAS
Surface water [mg/dm^3]				
$c_{min} \pm U(k = 2)$	< LOQ			
$c_{max} \pm U(k = 2)$	0.240±0.018	0.2105±0.0023	0.1983±0.0046	0.0546±0.0011
$\overline{C}$	0.075	0.057	0.044	0.019
SD	0.052	0.044	0.040	0.014
Bottom deposit [mg/kg of sample]				
$c_{min} \pm U(k = 2)$	< LOQ			
$c_{max} \pm U(k = 2)$	0.0784±0.0012	0.137±0.017	0.171±0.012	0.207±0.010
$\overline{C}$	0.037	0.070	0.096	0.111
SD	0.017	0.030	0.038	0.040

c_{min}; c_{max} - the lowest and the highest determined concentration of analytes, respectively; $\overline{C}$ - arithmetic mean of the determined concentration of a given analyte in all samples taken in a given season; SD - standard deviation
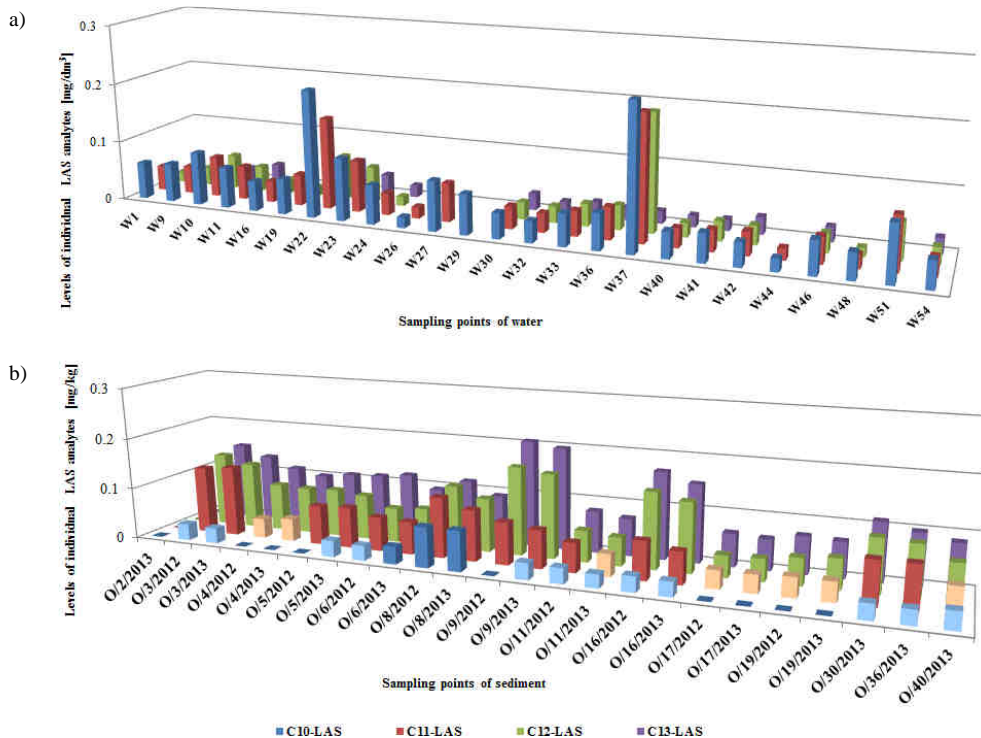

Fig. 3. Content levels of individual analytes from the LAS group in liquid (a) and solid (b) environmental samples (lighter bars in each series concern concentration values in the scope from > LOD to < LOQ) ([mg/dm^3] or [mg/kg], respectively)

In surface water samples analytes containing shorter alkyl chains in their molecules were mainly found and determined (hydrophilicity of surfactants increases). Maximum

determined concentrations of LAS compounds were within the range of 0.0546±0.0011 to 0.240±0.018 mg/dm^3, for C_{13}-LAS and C_{10}-LAS, respectively. In the analysed liquid samples average concentrations of selected anionic analytes were within the range of 0.019±0.014 to 0.075±0.052 mg/dm^3, for C_{13}-LAS and C_{10}-LAS, respectively.

In the case of test results of bottom sediment samples, the found and determined anionic surfactants were the ones with molecules built from longer alkyl chains. As in the case of liquid environmental samples, some samples of bottom sediments do not contain the analysed analytes. Maximum determined concentrations of LAS compounds are in the range between 0.0784±0.0011 and 0.207±0.010 mg/kg, for C_{10}-LAS and C_{13}-LAS, respectively. Average content of individual analytes from the anionic surfactants group in solid samples was determined in the range from 0.037±0.017 up to 0.111±0.040 mg/kg of the sample, for C_{10}-LAS and C_{13}-LAS, respectively. The relationship between the content of LAS compounds determined in solid and liquid environmental samples and their place of collection is presented in Figure 3.

In the case of liquid samples labelled W22 and W37 we may suppose that they have been collected in areas with the greatest pollution in the researched ecosystem. On the other hand, samples of surface water labelled in the present study as W26 and W44 are the least polluted by analytes from the LAS group. Solid environmental samples labelled as O3, O9 and O16 contain the highest concentrations of the determined compounds from the LAS group. On the other hand, in samples labelled O2, O17 and O19 some anionic analytes were not found or they were determined at very low concentration levels.
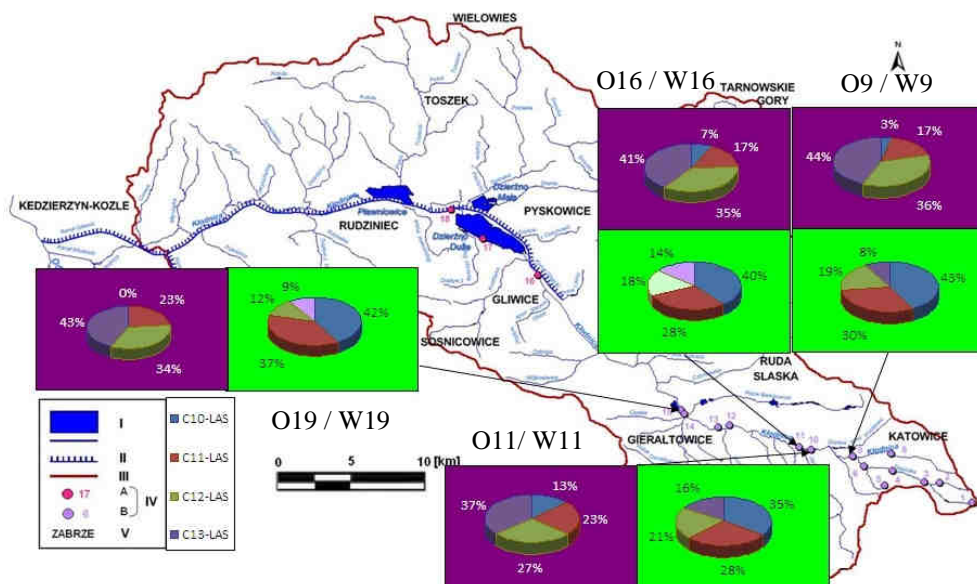

Fig. 4. Percentage relationship between the levels of concentrations of certain anionic surfactants and their summary content in liquid and solid samples collected in the same area (green colour - water samples collected in the period 2010-2012 and 2013; purple colour - samples of deposits collected in 2012 and 2013)

Percentage relationship between concentration levels of certain anionic surfactants in liquid and solid samples collected in the same catchment area of the Klodnica river is presented in Figure 4.

Comparing the obtained percentage values of certain anionic surfactants with summary levels of their concentrations determined in environmental samples it can be stated that these relationships are similar for most batches of the tested samples. Higher concentrations of C_{10}-LAS and C_{11}-LAS analytes were determined in liquid samples. And higher levels of C_{12}-LAS and C_{13}-LAS surfactant content were determined in solid samples.

In the literature, there are described only few studies concerning compounds from the group of LAS (Table 7) [6, 8, 22].

Table 7

Determination of individual LAS in environmental samples

Type of sample/origin		Concentration ranges of the analysed compounds	Literature
river sediments		0.95-11.15 µg/kg	[8]
		293-1938 µg/kg	[6]
water	lake	10.7-17.4 µg/dm^3	
	river	6-204 µg/dm^3	[22]
	sea	4-24 µg/dm^3	

For the river polluted mainly with sewage effluent and industrial waste, the mean concentration of total homologues and isomers of LAS was significant: 0.224 mg/dm^3 [22]. Obtained values are at the same level as the highest concentrations in the samples from the Klodnica River. Sea water samples collected from the harbour where river water taken from were analysed at different times of the year. The mean concentration of total homologues and isomers of LAS was found to be 0.058 mg/dm^3 and it is approximately four times lower [22]. Whereas in the samples of river sediments, concentrations of a group of LAS is approximately 10 times higher [6] which is also observed for water and sediments samples collected from the Klodnica River.

Conclusions

Selected anionic surfactants were determined in samples of water from the Klodnica river (25 samples) and bottom sediments (25 samples). In most samples the presence of anionic analytes was confirmed. The determined concentration levels were in the range of up to 0.2105±0.0023 mg/dm^3 or 0.207±0.010 µg/kg (surface water and bottom sediment samples, respectively). Comparing the concentrations of certain analytes found in liquid and solid environmental samples, it can be noticed that the surfactants containing a shorter alkyl chain in a molecule were present in higher concentrations in liquid samples (hydrophobicity increasing with the increasing length of the chain) and the other way round. Therefore, lower content levels of compounds from the C_{12}-LAS and C_{13}-LAS group in surface water samples can be the result of sorption processes on the surface of solid particles of bottom sediments. And these analytes occur in higher concentrations in solid environmental samples. Few studies described in the literature confirm these findings.

Acknowledgements

References

[1]   Ying GG. Environ Inter. 2006;32:417-431. DOI: 10.1016/j.envint.2005.07.004.

[2]   Pastewski S, Mędrzycka K. Pol J Environ Stud. 2003;12:643-646. www.pjoes.com/pdf/12.5/643-646.pdf.

[3]   Olkowska E, Ruman M, Kowalska A, Polkowska Ż. Ecol Chem Eng S. 2013;20:331-342. DOI: 10.2478/eces-2013-0024.

[4]   Lara-Martin PA, Gomez-Parra A, Gonzalez-Mazo E. J Chromatogr A. 2006;1114:205-210. DOI: 10.1016/j.chroma.2006.03.014.

[5]   Fendinger NJ, Versteeg DJ, Wee GE, Dye RS, Rapaport RA. Environmental behaviour and fate of anionic surfactants. In: Baker LA, editor. Environmental Chemistry of Lakes and Reservoirs. ACS Advances in Chemistry Series No. 237. Washington DC, United States: American Chemical Society; 1994.

[6]   Lara-Martin PA, Gomez-Parra A, Gonzalez-Mazo E. Environ Pollut. 2008;156:36-45. DOI: 10.1016/j.envpol.2008.01.005.

[7]   Zhao Z, Xie Z, Möller A, Sturm R, Tang J, Zhang G, et al. Environ Pollut. 2012;170:71-77. DOI: 10.1016/j.envpol.2012.06.004.

[8]   Sanderson H, Dyer SD, Price BB, Nielsen AM, van Compernolle R, Selby M, et al. Sci Total Environ. 2006;368:695-712. DOI: 10.1016/j.scitotenv.2006.04.030.

[9]   Andreu V, Picó Y. Anal Chem. 2004;76:2878-2885. DOI: 10.1021/ac035483e.

[10] Clara M, Scharf S, Scheffknecht C, Gans O. Water Res. 2007;41:4339-48. DOI: 10.1016/j.watres.2007.06.027.

[11] Sanchez-Martinez ML, Aguilar-Caballos MP, Eremin SA, Gomez-Hens A. Talanta. 2007;72:243-248. DOI: 10.2174/1386207311316060010.

[12] Nomura Y, Ikebukuro K, Yokoyama K, Takeuchi T, Arikawa Y, Ohno S, et al. Biosens Bioelectron. 1998;13:1047-53. DOI: 10.1016/S0956-5663(97)00077-8.

[13] Jensen J. Sci Total Environ. 1999;226:93-111. DOI: 10.1016/S0048-9697(98)00395-7.

[14] Paria S. Adv Colloid Interface Sci. 2008;138:24-58. DOI: 10.1016/j.cis.2007.11.001.

[15] Szymański A, Wyrwas B, Jesiołowska A, Kaźmierczak S, Przybysz T, Grodecka J, et al. Pol J Environ Stud. 2001;10:371-376. http://www.pjoes.com/.

[16] Czaja S, Rahmonov O, Wach J, Gajos M. Pol J Environ Stud. 2014;23:629-637. http://www.pjoes.com/pdf/23.2/Pol.J.Environ.Stud.Vol.23.No.2.629-637.pdf.

[17] Ruman M, Olkowska E, Kozioł K, Absalon D, Matysik M, Polkowska Ż. J Environ Qual. 2014;43:753-62. DOI: 10.2134/jeq2013.06.0225.

[18] Olkowska E, Kudłak B, Tsakovski S, Ruman M, Simeonov V, Polkowska Ż. Sci Total Environ. 2014;476:477-484. DOI: 10.2478/eces-2013-0033.

[19] Nagarnaik PM, Mills MA, Boulanger B. Chemosphere. 2010;78:1056-62. DOI: 10.1016/j.chemosphere.2009.11.019.

[20] Merino F, Rubio S, Pérez-Bendito D. Anal Chem. 2003;75:6799-806. DOI: 10.1021/ac030224a

[21] Nenpo K. Annual Report of Tokyo Metropolitan Research Laboratory of Public Health, 1972;24:397. www.tokyo-eiken.go.jp/assets/issue/journal/1-50/index-e.html.

[22] Akyuz M. Talanta. 2007;71:471-478. DOI: 10.1016/j.talanta.2006.06.0.