Limnol. Rev. (2017) 17, 1: 11–21
DOI 10.1515/limre-2017-0002

DE GRUYTER
OPEN

Selected anionic and cationic surface active agents: case study on the Kłodnica sediments

Ewa Olkowska[1], Marek Ruman[2], Magdalena Drąg-Śmigalska[3], Żaneta Polkowska[4]

[1]Department of Environmental Toxicology, Faculty of Health Sciences with Subfaculty of Nursing and Institute of Maritime and Tropical Medicine, Medical University of Gdansk, Debowa 23, 80-204 Gdansk, Poland, e-mail: ewa.olkowska@gumed.edu.pl (corresponding author)
[2]Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland, e-mail: marek.ruman@us.edu.pl
[3]Faculty of Earth Sciences, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland, e-mail: magdalena.ewa.drag@gmail.com
[4]Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland, e-mail: zanpolko@pg.gda.pl

Abstract: Surface active agents (surfactants) are a group of chemical compounds, which are used as ingredients of detergents, cleaning products, cosmetics and functional products. After use, wastes containing surfactants or their degradation products are discharged to wastewater treatment plants or directly into surface waters. Due to their specific properties of SAAs, compounds are able to migrate between different environmental compartments such as soil, sediment, water or even living organisms and accumulate there. Surfactants can have a harmful effect on living organisms. They can connect with bioactive molecules and modify their function. Additionally, they have the ability to migrate into cells and cause their damage or death. For these reasons investigation of individual surfactants should be conducted. The presented research has been undertaken to obtain information about SAA contamination of sediment from the River Kłodnica catchment caused by selected anionic (linear alkylbenzene sulfonates (LAS C_{10}-C_{13})) and cationic (alkylbenzyldimethylammonium (BDMA-C_{12-16}), alkyl trimethyl ammonium (DTMA), hexadecyl piridinium chloride (HP) chlorides) surfactants. This river flows through an area of the Upper Silesia Industrial Region where various companies and other institutions (e.g. coal mining, power plants, metallurgy, hospitals) are located. To determine their concentration the following analytical tools have been applied: accelerated solvent extraction– solid phase extraction – high performance liquid chromatography – UV-Vis (anionic SAAs) and conductivity (cationic SAAs) detectors. In all sediments anionic SAAs have been detected. The concentrations of HTMA and BDMA-C_{16} in tested samples were higher than other cationic analytes. Generally, levels of surfactants with longer alkyl chains were higher and this observation can confirm their higher susceptibility to sorption on solid surfaces.

Key words: surface active agents, sediment, the River Kłodnica

Introduction

In surface waters a wide range of organic compounds of various origins can occur. Compounds from natural sources can be: humus substances, chlorophyll, metabolites of living organisms, compounds derived from the decomposition of dead parts of plant and animal tissues. Human activities are responsible for the introduction of organic pollutants such as pesticides, phenols, mono- or polycyclic aromatic hydrocarbons, phthalates, organic dyes, surfactants, petroleum products, oils, fats and many others to the aquatic environment. These substances sometimes enter the surface waters unintentionally, due to pipeline failure, oil tanker catastrophe or industrial accidents. Unfortunately, in most cases they are introduced with untreated or poorly treated sewage, with the effluents of mining heaps or solid waste landfills and directly through the use of plant protection agents and fertilizers (Hermanowicz et al. 1999; Staszewski 1990; Namieśnik 1992).

The above mentioned surface active agents (SAAs) are compounds which contain hydrophilic and hydrophobic parts in their molecules. If they have a charge on the hydrophilic part they can be classified into the anionic (negative) or cationic (positive) group of SAAs. If they contain both charges SAAs are known as amphoteric compounds. In the case of a lack of charges surfactants are classified as non-ionic (Fig. 1).

Because of its chemical structure, three main groups of detergents are distinguished: anionic, cationic and

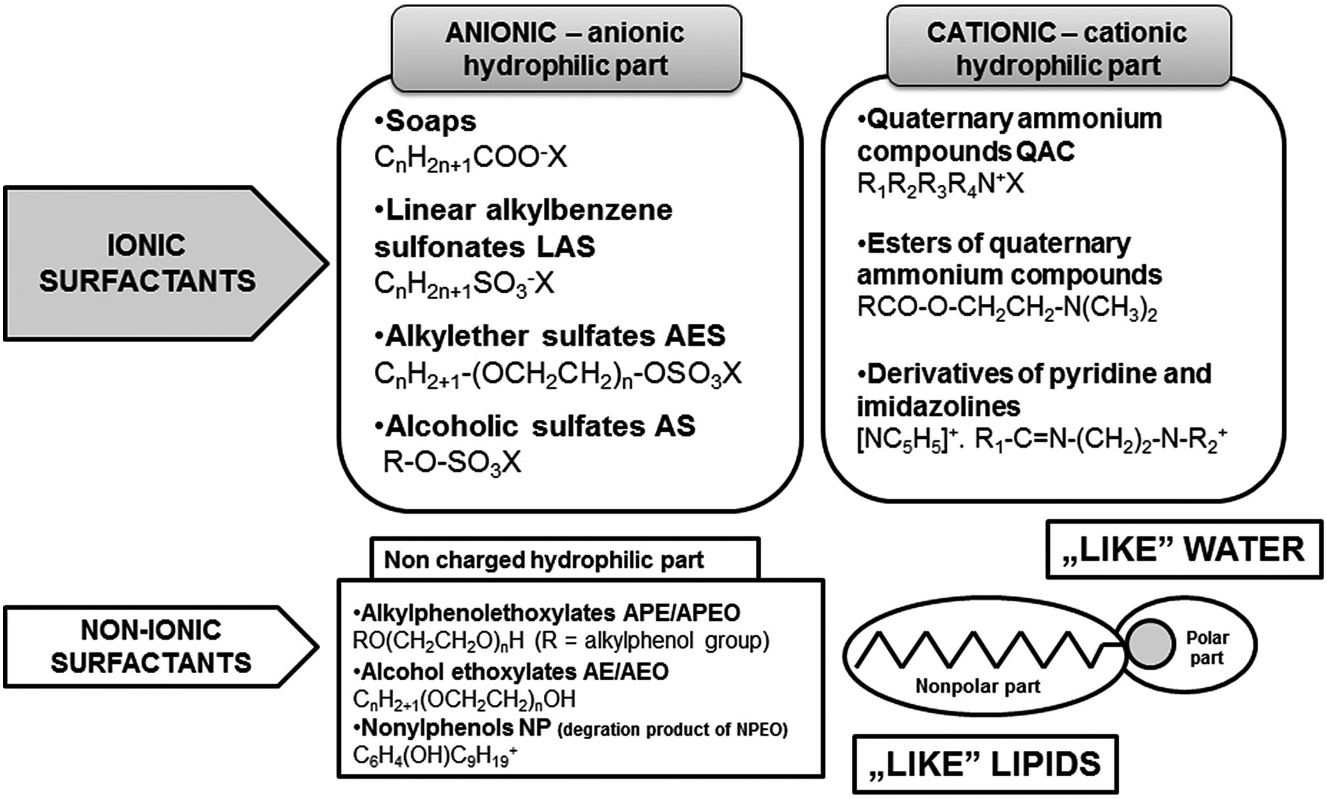

Fig. 1. Classification of surfactants due to structure of their molecules

non-ionic. Another division is based on biodegradability. The first chemical group is non-foamable and easily biodegradable ('soft surfactants'). These are mostly straight-chain alkylbenzene sulfonates (e.g. linear alkylbenzene sulfonates, LAS). "Hard" surfactants are primarily alkylbenzene sulfonates with an alkyl branched alkyl chain (ABS). They form durable foam and do not undergo degradation in the biological stage in wastewater treatment plants (WWTPs). Stable foam in an effluent waste stream is a serious technological problem for the WWTPs (causes resistance to sand filters, impedes coagulation and sedimentation processes). Moreover, in the environment the foam interferes with the process of self-cleaning water. Surface active agents exert a toxic effect on the water body biocenosis. Nitrifying bacteria are especially sensitive to surfactants while Gram-negative bacteria tolerate higher concentrations of SAA than Gram-positive bacteria (there are also bacteria that use SAAs as a source of carbon, thus reducing pollution). Some surfactants can be harmful compounds to algae, fish and other aquatic organisms. What is more, their degradation products can have a negative impact on living organism. SAAs are able to accumulate in animal and human tissues and organs and they can influence the structure of protein, cause allergies and skin irritation. Indirectly, surfactants affect plants and animals because they simplify the dissolution of hazardous toxins such as PAHs and pesticides and facilitate their accumulation in the body. The most toxic SAAs are cationic, the least nonionic (Hermanowicz et al. 1999; Staszewski 1990; Namieśnik 1992).

The chemical structure of SAAs is connected with the occurrence of properties such as the possibility of their dissolving in polar and non-polar medium, ability to form micelles and sorption on phase boundaries. Due to their specific structure and properties they can be used in a number of ways (e.g. as detergents, cosmetics, fabric softener, disinfection products etc.). The areas in which different types of surfactants are commonly used are presented in Table 1 (Myers 2005; Ying 2006; Traverso-Soto et al. 2012; Olkowska et. al. 2011; Nelson 1982; Schramm et al. 2003; Myers 2005; Plaza and Margielewski 2009; Sekhon 2013).

Currently, surfactants are used in almost all industrial activities. For example, in mining surfactants are used for dust removal from air in mining pavements or purification of coal in flotation processes to remove admixtures. The term flotation is now used to define foam flotation. Previously, oil and surface flotation was also distinguished.

The foam flotation process consists of several operations and separation in a flotation mixture containing finely ground minerals and water with additive agents (e.g. surfactants). Selective separation occurs through

Table 1. Areas of application of surface active agents (Nelson 1982; Schramm et al. 2003; Myers 2005; Plaza and Margielewski 2009; Sekhon 2013)

	Areas of SAAs application/ Products containing surfactants	Examples of SAAs group/compounds used in specific area
Household chemicals	– detergents, washing, cleaning and softening agents – anti-microbial agents – bleaching agents	linear alkylbenzene sulfonates (LAS) ethylene diamine tetraacetic acid ditallow dimethyl ammonium chloride (DTDMAC) alkanolamides
Cosmetics industry	– emulsifiers – foaming agents – dispersing agents – anti-microbes agents	sodium lauryl sulfate (SDS) alkanolamides lauryl acid amino acid (lauramide DEA)
Food industry	– emulsifiers – foaming agents – stabilizing agents	mono- and diglycerides derived from fats and oils lecithin and modified lecithins derivatives of ethoxylated fatty acid and sugar (primarily sorbitol)
Textile industry	– wetting and washing agents – dispersing agents – additives for fabric dyeing – supporting agents to produce synthetic textiles	sodium bis(2-ethylhexyl) sulfosuccinate nonylphenol ethylenoxide alkylsulfates alkylether sulfates
Petroleum, mining and metallurgical industry	– components of drilling fluids – corrosion inhibitors – anti-icing additives – deemulsifying agents for the desalination of crude oil – additives to petroleum products – cleaning agents of metal surfaces – agents used for enrichment of ores	polyalkoxy glycol dithiophosphates (PGDP) alkyldiamines alkylsuccinimides of diethylenetriamine alkylphenolic amines alkylimidazolines
Electronic industry	– preparation of superconducting materials – preparation of magnetic particles	anionic fluorochemical surfactant tetramethylammonium hydroxide lecithin
Medicine and pharmacological industry	– antiseptic agents – agents used in the manufacture of pharmaceuticals (cream and suspensions products) – synthetic pulmonary surfactants	benzalkonium chloride polysiloxanes dipalmitoylphosphatidylcholine hydroxypropyl methylcellulose alkyl polyglucosides polysorbate-type nonionic surfactant
Crop protection	– agents used in formulation of pesticides	ethoxylated alcohola alkylphenols sorbitan alkylamines
Other	– agents use in bioremediation of soil and wastes – ingredients of paints, coatings and adhesives	rhamnolipids octylphenoxy polyoxyethylene ethanol polyoxyethylene sorbitan monooleate

the use of different physicochemical properties of the surface of mineral particles, mainly their varying degrees of wettability (Konopacka 2005; Fuerstenau et al. 2007). A significant increase in the global consumption of surfactants has resulted in an increase in their concentration in wastewater discharged into the sewage system. The occurrence of surfactants in sewage causes the formation of foam. Moreover, foam formation has been observed in river waters located near large concentrations of population and industrial areas. In wastewater treatment plants they can be eliminated from the influent stream through various processes such as sorption and biodegradation. Unfortunately, for some surface active agents their degradation is only partial and sometimes they are directly released to surface waters (Ying 2006). It should be noted that the presence of surfactants and their biodegradation products in ecosystems can result in toxic effects on fish and other aquatic organisms, especially in the bottom zone. It is very important to conduct constant monitoring of the concentrations of surfactants in water and wastewater, especially anionic compounds which have the largest world production (~60%) (Ogonowski and Tomaszkiewicz-Potepa 1999; Zieliński, 2009; Strugała-Wilczek et al. 2013; Olkowska et al. 2014). The points mentioned above result in the emission of contaminants to the environment where they can freely migrate between components and undergo different physicochemical processes (e.g. sorption, biodegradation) (Olkowska et al. 2014) or become persistent pollutants (e.g. LAS under anaerobic conditions). Contamination of cationic surfactants are mainly associated with the solid phase (sediments) rather than the aqueous phase due to hydro-lipophilic and electrostatic interactions with nega-

Table 2. Toxicity of selected anionic and cationic surfactant for *Daphnia magna* (based on Ivanković and Hrenović 2010; Olkowska et. al. 2011; OECD 2005)

SAAs group	Compound	Acronym	Chemical formula	Log $K_{o/w}$	Toxicity param./ exposure time	Conc. [mg dm^{-3}]
Anionic	Na(C_{10} – linear alkylbenzene sulfonate)	LAS C10	$C_{10}H_{21}C_6H_4SO_3Na$	3.32 (LAS $C_{11.6}$) 1.96 (LAS C_{12})	LC_{50}/48 h	13.9
	Na(C_{12} – linear alkylbenzene sulfonate)	LAS C12	$C_{12}H_{25}C_6H_4SO_3Na$		LC_{50}/48 h	8.1
	Na(C_{14} – linear alkylbenzene sulfonate)	LAS C14	$C_{14}H_{29}C_6H_4SO_3Na$		LC_{50}/48 h	1.22
	sodium dodecylsulphonate	SDS	$NaC_{12}H_{25}SO_4$	1.6	EC_{50}/24 h	28.77
Cationic	tetradecyl trimethyl ammonium chloride	TMAC	C17H38ClN	N/A	IC_{50}/24 h	0.13–0.38
	benzyl dimethyl ammonium chloride	BDMAC	C9H14ClN	–2.17	EC_{50}/24 h	0.13–0.22
	ditallow dimethyl ammonium chloride	DTDMAC	Not available	N/A	LC_{50}/48 h	0.49

$K_{o/w}$ – octanol/water partition coefficient, LC_{50} – lethal concentration, EC_{50} – effect concentration, IC_{50} – inhibition concentration

tively charged surfaces (Martinez-Carballo et al. 2007). The properties of anionic surfactants (e.g. LAS) are related with the length of the alkyl chain and position on the functional group. It has been found that the longer the alkyl chain LAS homologues have, the higher the octanol/water partition coefficient ($K_{o/w}$). Such dependence will result in greater contamination of the solid phases of aquatic bodies with substances with a longer chain because they possess a greater ability for sorption on solids (Ying 2006; Sablayrolles et al. 2009; Olkowska et al. 2014).

Moreover, in various parts of ecosystems they can disturb the balance of processes such as cloud formulation, distribution of organic compounds and long distance transport of contamination (Ying 2006).

As it was previously mentioned surface active agents can have a different impact on living organisms. Compounds from the group of surfactants can be connected to bioactive molecules (e.g. peptides, enzymes) and such processes can lead to modification of biological function. Additionally, they can migrate into the cells of living organism and cause their damage or even death. Table 2 summarizes the acute toxic effects of anionic and cationic surface active agents on aquatic organisms like *Daphnia magna* (Cserháti et al. 2002; McDonell and Russel 1999; Ivanković and Hrenović 2010).

As a response to the excessive application of SAAs and their harmful effects on ecosystems and living organisms, monitoring of surfactants in the environment should be conducted and their concentration in different elements should be regulated. Moreover, they should be determined as individual components and not as total content. This approach is associated with their possible impact on determined values of SAAs using the spectrophotometry technique and their differences in physicochemical properties among the groups (Ying 2006; Nomura et al. 1998). In different research centers (USA, Japan, Spain, Portugal, Italy, Austria) determination of selected anionic and cationic surfactants in sediments has been conducted (OECD 2005; Hampel et al. 2009; Martinez-Carballo et al. 2007; Ferrer and Furlong 2002; Li and Brownawell 2010; Sun et al. 2003). In Poland determination of individual surfactants has only been conducted on a relatively limited scale (mainly liquid samples). The aim of presented research was to investigate levels of selected cationic and anionic surfactants in river bottom sediment samples from the River Kłodnica, Silesia Region.

Study area

The River Kłodnica is part of the Upper Oder river basin. Administratively it belongs to two voivodships Silesia and Opole; it has a total catchment area of approx. 1126 km^2. The boundary of the study (the upper catchment Kłodnica) is defined by the Kłodnica inlet into the Dzierżno Duże reservoir (Działoszyńska-Wawrzkiewicz 2007) (Fig. 2).

The biggest of the right-hand tributaries of the Kłodnica after the profile of the Gliwice water gauge are: Bujakowski stream, Czarniawka, Bytomka with the Mikulczycki stream, Drama and Toszecka stream. Those on the left-hand are: the streams Ślepiotka, Jamna and Promna. In the Kłodnica catchment there are three artificial reservoirs: Dzierżno Duże on the River Kłodnica, Dzierżno Małe on the River Drama and Pławniowice on the Toszecki Stream. All reservoirs are located below the Gliwice profile, which closes the highly urbanized part of the catchments. The further course of the Kłodnica drains mostly agricultural areas (Nocoń et al. 2006; Drąg and Zimnol 2014). Economic activity and development of urbanization have affected not only the physical parameters of the valleys, but also other elements of the conditioning hydromorphological watercourses (Hamerla and Pierzchała 2016). The Kłodnica catchment is a heavily polluted water system located in the region of the Upper Silesian Industrial District (USID). The Kłodnica is located in an area where different forms of human activity exist (e.g. underground coal mining, metallurgy, a power generation plant, discharges of untreated sewage directly into the river). Mine water from many working mines ("Silesia" (be-

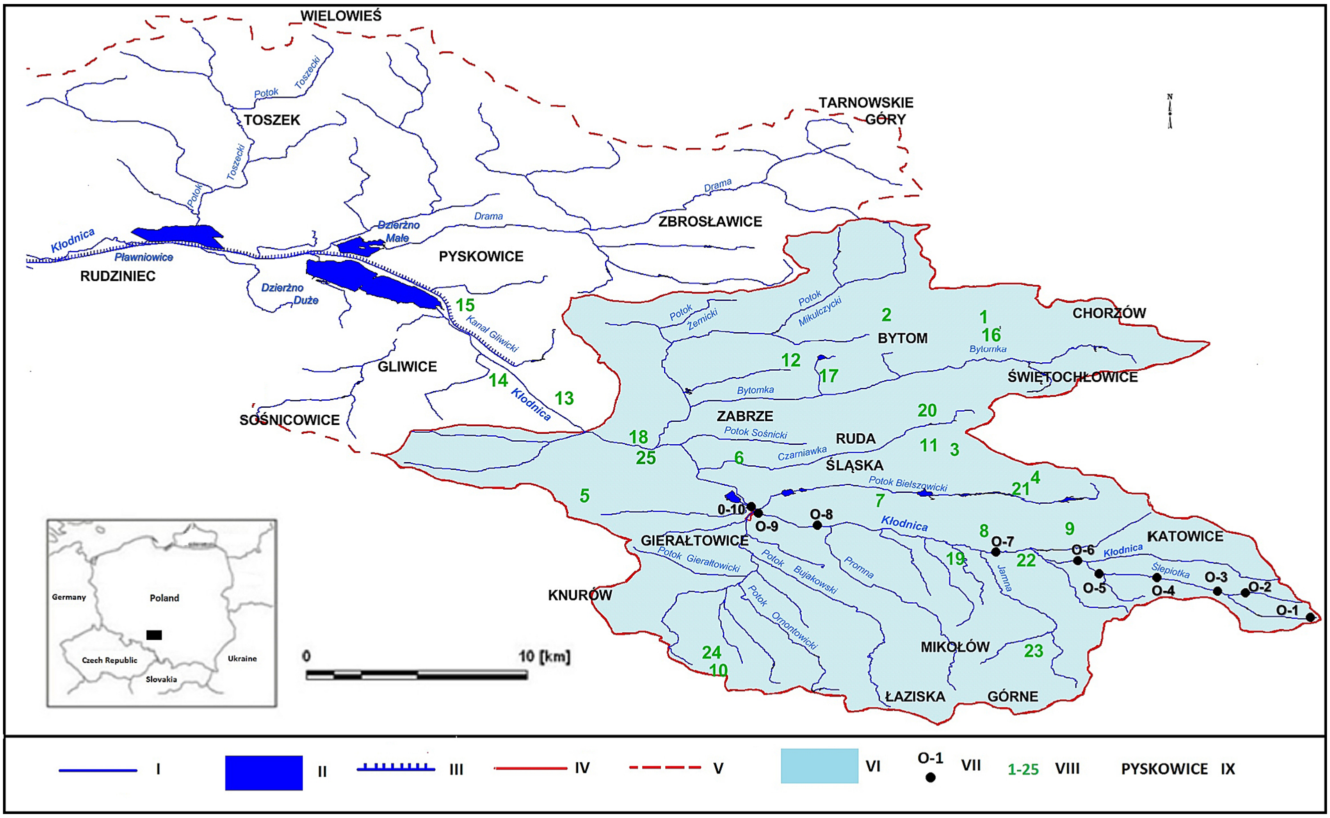

Fig. 2. Description of the area and sampling points: I – watercourses, II – reservoirs, III – canals, IV– the border of the Kłodnica catchment, V – the border of the Kłodnica catchment to Kłodnica profile, VI – the border of the Kłodnica catchment to Gliwice profile, VII – bottom sediment sampling points, VIII – localization of pollution points and wastewater treatment plants (1–10) – coal-mining industry, (11–13) – smelters, (14,15) – transport industry, (16–19) – the energy industry, (20) – chemical industry, (21–25) – wastewater treatment plants), IX – cities

longing to Katowicki Holding Węglowy S.A.), "Halemba", "Polska-Wirek", "Zabrze-Bielszowice", "Pokój", "Makoszowy", "Sośnica" (belonging to Kompania Węglowa S.A.) and mining plants is discharged directly into the Kłodnica River catchment. The catchment also encompasses an area of Bytom where there are a number of mines that have closed ("Centrum", "Bytom III" and "Bytom II") (Magdziorz and Lach 2001), where sewage was also emitted into river water. The mines located in the basin of the Kłodnica are among the oldest in the whole USID. They are currently undergoing a restructuring phase, due to the termination of exploitation of some mining areas or complete liquidation. To date, the following mines, or parts of them, (7) have been closed: "Pstrowski", "Gliwice", "Siemianowice" – ZG "Rozalia", "Ruch Polska" – "Polska-Wirek", "Ruch Poręba" – "Bielszowice", "Ruch Halemba Płytka" – "Halemba", "Ruch Wawel" – "Pokój". It should be mentioned that in the case of liquidated mines in area of the Bytomka catchment dewatering is also applied so as to ensure the safety of active mines (Lach et al. 2004). The impact of pollution from industrial and municipal areas on this ecosystem is observed as changes in the hydrographic network of rivers and the quality of its waters (Trochim 2006; Ruman et al. 2014). As a consequence of the previously mentioned aspects the River Kłodnica was selected as a research area. Sampling points were chosen to determine the nature of the river and the impact of individual tributaries or wastewater discharging points (including the content of surface-active compounds). Moreover, they were located above and below points of waste discharge from plants into tributaries, and above and below the outlet of the tributaries after their mixing with the water of the Kłodnica. Thus, the river can be presented as an example of a highly contaminated aquatic ecosystem. The river flows through two different sozologically distinct areas that were separated by the location of the bottom sediment sampling points. The bottom sediment samples were collected at ten points. The location of sampling stations in the River Kłodnica catchment is presented in Figure 2. A description of the location of sampling points is given in Table 3.

The location of the bottom sediment sampling was also determined by the depth of the river, the currents and the height of the bank in the given cross section along the mouth of the Kłodnica to the River Oder,

Table 3. Information about sampling points

Sampling point	Description of sampling points	City / City district
O-1	Ślepiotka Stream – source	Katowice/Murcki
O-2	Ślepiotka Stream – tributary No. I	Katowice/Ochojec
O-3	Ślepiotka Stream – below the mouth of tributary No. I	Katowice/Ochojec
O-4	Ślepiotka Stream – Zadole settlement	Katowice/Piotrowice
O-5	Ślepiotka Stream – below the mouth of tributary No. II	Katowice/Wymysłów
O-6	Kłodnica River – below the mouth of Ślepiotka Stream	Katowice/Panewniki
O-7	Kłodnica River – above the mouth of Jamna Stream	Ruda Śląska/Stara Kuźnia
O-8	Kłodnica River – below the mouth of Promna Stream	Zabrze/Makoszowy and Gierałtowice/Przyszowice
O-9	Kłodnica River – above the mouth of Bujakowski Stream	
O-10	Kłodnica River – below the mouth of Bujakowski Stream	

which provided for the availability of sampling. Points of sample collection were divided into two groups. The first set of samples were collected only in the first tributary of the Kłodnica the – Ślepiotka Stream (points O-1 to O-5). The second group of sampling points was located in the area of the main tributaries of the Kłodnica, where the level of industrial activity is very high (points O-6 to O10). Most samples from the second set were collected above the inlet zones of the tributaries (O-7 to O-9). Sample O-10 represents the area below the inlet zones of the tributaries.

Methods

The sediment samples (about 2 kg) were collected manually using a stainless steel scoop. This allowed a surface layer of sediment of up to 30 cm in depth to be collected (depending on the conditions). Sampling was carried out on one day. The sediments were then transported to the laboratory and dried at room temperature. Dried samples were sieved through a nylon sieve (2 mm mesh size) to eliminate non-sediment materials such as pieces of wood, pieces of metal scrap, slag fragments, paint and paint crumbs, solidified pieces of tar or asphalt etc. To prepare material for analysis (<0.063 mm), a 100 g sample of a fraction <2 mm was homogenized and milled in agate mortar. Such samples were used to determine levels of cationic and anionic surfactants.

All chemical reagents for the research were supplied by Merck KGaA (Germany). The solid phase extraction (SPE) cartridges applied in the experiments were made by Phenomenex (USA). Standards of selected anionic and cationic surface active agents: dodecylbenzyldimethylammonium chloride (BDMA-C_{12}), tetradecylbenzyldimethylammonium chloride (BDMA-C_{14}), hexadecylbenzyldimethylammonium chloride (BDMA-C_{16}), dodecyltrimethylammonium chloride (DTMA), hexadecyltrimethylammonium chloride (HTMA), hexadecylpiridinium chloride (HP) and linear alkylbenzene sulfonates (LAS C_{10}-C_{13}) were purchased from Sigma-Aldrich (Germany).

To isolate anionic and cationic surfactants from sediment samples the accelerated solvent extraction technique (ASE) was applied. Extraction was performed in a Dionex ASE 350 device (Thermo Scientific, USA). Three extraction cycles were conducted for 15 min (T=100°C) (Olkowska et. al 2012; Traverso-Soto et al. 2013) with the use of mixtures of acetonitrile-water and methanol-water in the case of cationic and anionic surfactants, respectively. During the following stage, the obtained extracts were cleaned up with solid phase extraction. For extracts with anionic SAAs cartridges with Strata C18-E (solvent for conditioning, washing and elution: methanol-water) were used. Recovery of LAS after applying the proposed protocol ranged between 89–101%. In the case of cationic analytes cartridges, known as Strata-X (solvent for conditioning, washing and elution: acetonitrile-water-acetic acid) were applied to clean up the extracts. Recovery of determined cationic SAA ranged from 83 up to 98%.

The C_{10}-C_{13} linear alkylbenzene sulfonates were separated using an *Acclaim Surfactant Plus®* column (Thermo Scientific, USA) with a mobile phase acetonitrile-ammonium acetate buffer. Anionic surfactants were determined using ultraviolet-visible spectrophotometry (UV-Vis, 225 nm). Cationic surfactants were separated by means of an *Acclaim Surfactant®* (Thermo Scientific, USA) with mobile phase acetonitrile-acetic acid and acetonitrile-formic acid-water. A condutometric detector (CD) with two different suppressors (CMMS 300 and CSRS 300, Thermo Scientific, USA) was applied (Olkowska et al. 2013). All chromatographic analysis were performed using a high performance liquid chromatographer (HPLC, ICS-3000 system, Thermo Scientific, USA). The stages of applied analytical protocols are shown in Figure 3.

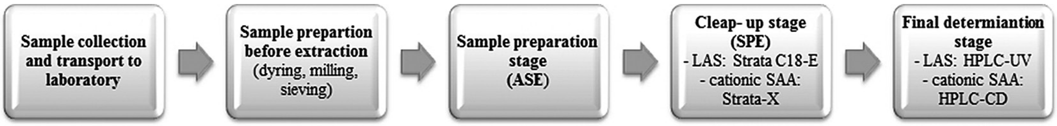

Fig. 3. Stages of applied protocols for determination of anionic and cationic surfactants

To estimate levels of LAS compounds the ASE-SPE-HPLC-UV-Vis procedure was applied. The detection limits for sediment samples were estimated from 5.3 to 16 μg kg^{-1}. For all anionic surfactants good correlation coefficients were obtained. To determine cationic surfactants the ASE-SPE-HPLC-CD procedure was used. The method's limit of detection (signal to noise ratio >3:1) of cationic SAA was calculated from 6.4 up to 29 μg kg^{-1}. For all analytes good correlation coefficients were received. Limits of detection for both groups of SAA were calculated using the equation LOD = 3.3×SD/b (where: b – the slope of the calibration curve; SD – standard deviation of the curve).

Results and discussion

Determination of linear alkylbenzene sulphonates in environmental samples is very important because they are frequently applied in various areas of human activities. The LAS concentration in sediments is presented in Figure 4.

Anionic surfactants were detected in all sediments. The concentration of individual compounds from the group of LAS for sediments ranged from below MDLs up to ~2100 μg kg^{-1}. The determined concentration of individual LAS in sediment collected in the Kłodnica catchment area is relatively similar to research conducted in Portugal (Hampel et al. 2009). Moreover, the trend that a higher concentration was determined for compounds with longer alkyl chains can clearly be observed. Research result confirm that LAS C_{12} and LAS C_{13} (more hydrophobic compounds than LAS C_{10} and LAS C_{11}) have greater sorption ability on the solid phase (sediment) in aquatic ecosystems (Ying 2006; Sablayrolles et al. 2009; Olkowska et al. 2014). At sampling points O-1, O-6 and O-8 levels of determined anionic surfactants were highest. This could be correlated with the presence of WWTP and other companies in these areas (see section *Study area* and Fig. 2). In other research (Table 4) measured LAS levels (total concentration) in sediments were generally less than 1–2 mg kg^{-1} dry weight (OECD 2005) with maximum concentration 230 mg kg^{-1} d.w. at sampling points close to untreated urban waste water effluent (Petrovic et al. 2002).

Compounds from the group of LAS are commonly used in different fields of human activity, they are found, for example, in household and industrial detergents, laundry agents, cosmetic ingredients. Their degradation processes in WWTPs are not completed (the highest efficiency 99%) and they can reach river water and accumulate in bottom sediments. As a consequence, benthic organisms may be exposed to anionic SAA, which can have harmful effects including lowered resistance to environmental conditions, disturbance of

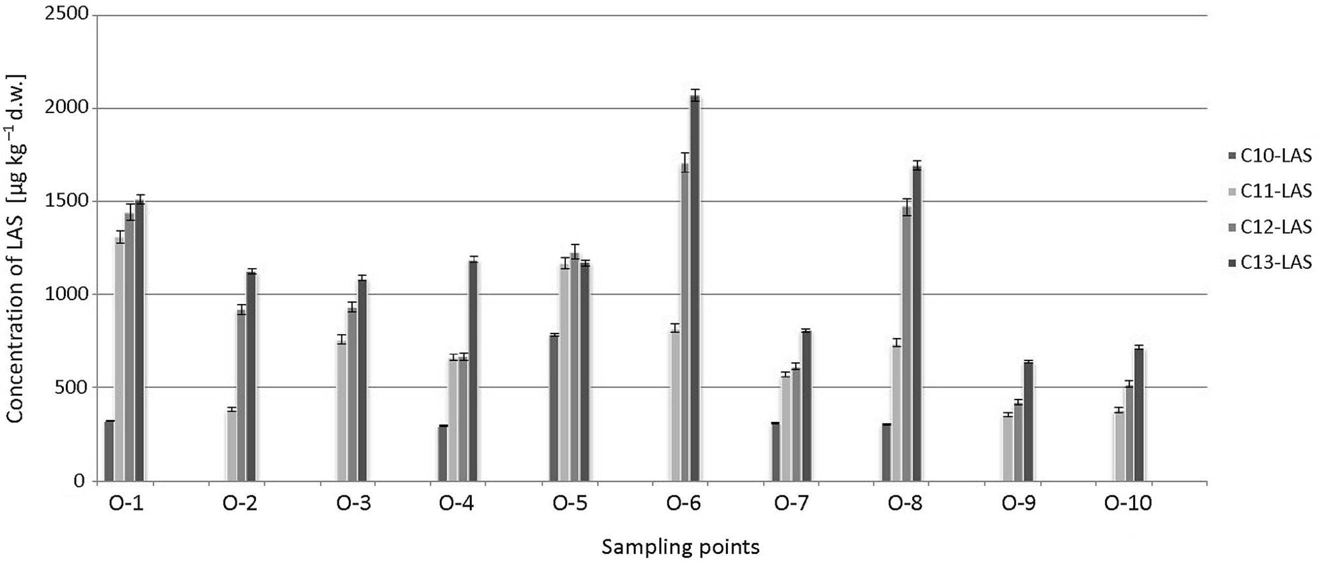

Fig. 4. The contents of anionic SAAs in the sediment samples

Table 4. The concentrations of LAS and determined cationic surfactant in different sediment samples

Research area	Compound	Concentration [µg kg^{-1}]	Reference
		Linear alkylbenzene sulfonates	
USA – Mississippi River	LAS	10-950	Tabor and Barber 1996
USA – Rapid Creek	LAS ~$C_{11.5}$	5300–11200	Rapaport and Eckoff 1990
Italy – Tiber River	LAS	up to 1800	DiCorcia et al. 1994
Spain – marine sediment	LAS	10–230000	Petrovic et al. 2002
Portugal – Tagus estuary	LAS C_{10}	up to 2600	Hampel et al. 2009
	LAS C_{11}	up to 3300	
	LAS C_{12}	up to 3500	
	LAS C_{13}	up to 1400	
		Cationic SAA	
Japan – river sediment	QAC	6200–69000	Utsunomiya et al. 1989
Japan – river sediment from Toyama City	QAC	500 times higher than in water	Sun et al. 2003
Austria – river sediment	BDMA-C_{12}	6–3600	Martinez-Carballo et al. 2007
	BDMA-C_{14}	n.d. – 1600	
	BDMA-C_{16}	1–350	
	DTMA	n.d. – 49	
	HTMA	<LOQ – 560	

reproduction, competitive stress, lower ability to degrade chemicals etc. (Hampel et al. 2009).

Generally, for positively charged surface active agents low biodegradability can be observed and their degradation products can be more toxic than their initial compounds. Furthermore, cationic compounds, which contain a positive charge in their molecules, can be sorbed to negatively charged solid surfaces like soil, sediments or tissues (Ying 2006; Olkowska et al. 2014). Therefore, it is necessary to understand the environmental fate of cationic SAAs. The levels of individual cationic SAAs in sediment samples are presented in Figure 5.

The concentrations of HTMA and BDMA-C_{16} were higher than other cationic analytes. Sampling points O-3 and O-8 are located in areas with the highest concentration (~1 mg kg^{-1} d.w.) of positively charged analytes. In other areas where samples were collected the levels of cationic SAA were not higher than 0.5 mg kg^{-1}. Determined concentrations of analytes were relatively higher than the values obtained in research conducted in Austria (Martinez-Carballo et al. 2007). The occur-

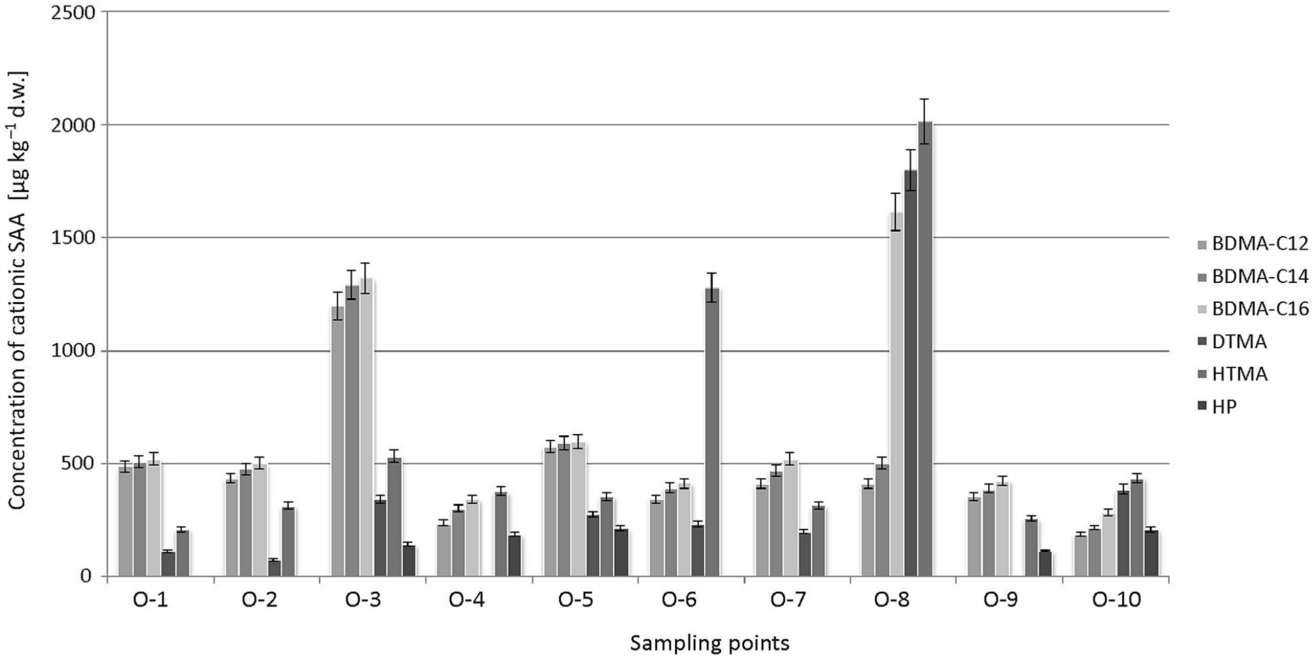

Fig. 5. The contents of cationic SAAs in the sediment samples

rence of cationic SAA can have a negative influence on living organisms according to their biocidal properties. The levels of surface active agents with longer alkyl chains were generally higher, thereby confirming their susceptibility for sorption on solid surfaces (Sablayrolles et al. 2009; Olkowska et al. 2014). Based on a literature review it can be observed that research on the concentration of anionic and cationic surfactants in sediment samples should be continued due to the lack of data. Such research data can be applied in environmental risk assessment, remediation activities and management of river catchments.

Conclusion

The various areas of application and the specific properties of surface active agents make it necessary to investigate their environmental fate and to obtain information necessary for environmental or health risk assessment. Traditionally, cationic and anionic SAAs are isolated with the use of *Soxhlet* and liquid-liquid extraction. To monitor highly polluted aquatic ecosystems such analytical tools are useless. Newly developed analytical procedures offer the possibility to replace these techniques and change them to greener and less-time consuming solutions. A fast and inexpensive protocol can be applied as the first step to protect ecosystems (reconnaissance phase of environmental problem) and at further stages of remediation processes.

The presented research results indicate that in river ecosystems highly contaminated with heavy metals and persistent organic pollutants, as examplified by the River Kłodnica, other chemical compounds can also be detected. The occurrence of cationic and anionic surfactants can have a negative impact on living organisms and natural processes in aquatic ecosystems. This group of compounds can present a considerable danger as they are able to freely migrate between the atmosphere, various types of aquatic ecosystems and sediments, soil or living organisms. To our knowledge, the investigation of selected anionic and cationic SAAs in sediment from the River Kłodnica is one of the first to be carried out in Poland. The conducted research shows that the river catchment located in an industrial area is also contaminated by organic compounds from the group of surfactants. Due to the damaging aspects of these compounds as well as the lack of official regulations for acceptable levels of individual cationic and anionic surfactants in elements of aquatic ecosystems determination of SAAs in environmental samples is has become a high priority. The data obtained in this investigation can help to support sustainable development, remediation processes or estimation of risk connected to high industrial activity in the area of the River Kłodnica.

Acknowledgments

This work was financially supported by the Polish Ministry of Science and Higher Education (project ST – 02-0103/07 and MN – 01-0211/08/322).

References

Cserháti T., Forgács E., Oros G., 2002, Biological activity and environmental impact of anionic surfactants, Environ. Int. 28(5): 337–348.

DiCorcia A., Samperi R., Belloni A., Marcomini A., Zanette M., Lemr K., Cavalli L., 1994, LAS pilot study at the “Roma-Nord” sewage treatment plant and in the Tiber river, Riv. Ital. Sostanze Gr. 71: 467–475.

Drąg M., Zimnol J., 2014, The evaluation of the state of environment under a strong human impact on the basis of SWOT analysis, AIP Conference Proceedings 1618: 281–284.

Działoszyńska-Wawrzkiewicz M., 2007, Koncepcja przyrodniczo-społecznego wykorzystania zalewisk na przykładzie zlewni rzeki Kłodnicy (The concept of natural and social use of flooding areas on the example of Kłodnica River) [typescript], Instytut Ekologii Terenów Uprzemysłowionych, Katowice, 47 pp (in Polish).

Ferrer I., Furlong, E.T., 2002, Accelerated solvent extraction followed by on-line solid-phase extraction coupled to ion trap LC/MS/MS for analysis of benzalkonium chlorides in sediment samples, Anal. Chem. 74(6): 1275–1280.

Fuerstenau M.C., Jameson G., Yoon R.H. (eds), 2007, Froth flotation: a century of innovation, Society of Mining, Metallurgy and Exploration (SME), Littleton, 879 pp.

Hamerla A., Pierzchała Ł., 2016, Ocena warunków hydromorfologicznych zurbanizowanych dolin rzecznych na przykładzie zlewni Kłodnicy (Hydromorphological assessment of urban river valleys of the Kłodnica catchment), Prz. Nauk. Inż. Kształt. Środ. 25(1): 83–99.

Hampel M., Canário J., Branco V., Vale C., Blasco J., 2009, Environmental levels of Linear alkylbenzene Sulfonates (LAS) in sediments from the Tagus estuary (Portugal): environmental implications, Environ. Monit. Assess. 149: 151–161.

Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B., Zerbe J., 1999, Fizyczno-chemiczne badanie wody i ścieków (Physical-chemical examination of water and wastewater), Wydaw. Arkady, Warszawa, 556 pp (in Polish).

Ivanković T., Hrenović J., 2010, Surfactants in the environment, Arh. Hig. Rada Toksikol. 61: 95–110.

Konopacka Ż., 2005, Flotacja mechaniczna (Mechanical flotation), Ofic. Wydaw. PWroc, Wrocław, 84 pp (in Polish).

Lach R., Magdziorz A., Maksymiak-Lach H., 2004, Zmiany jakości wód powierzchniowych zlewni Górnej Odry w wyniku restukturyzacji górnictwa węgla kamiennego (Changes in the quality of surface waters of Upper Oder catchment area as a result of restructuring of coal mining), Pr. Nauk. GIG "Górnictwo i Środowisko" 3: 53–70 (in Polish).

Li X.L., Brownawell B.J., 2010, Quaternary ammonium compounds in urban estuarine sediment environments e a class of contaminants in need of increased attention?, Environ. Sci. Technol. 44: 7561–7568.

Magdziorz A., Lach R., 2001, Zrzuty wód kopalnianych do wód powierzchniowych dorzeczy Odry i Wisły w województwie śląskim – charakterystyka stanu i prognozy (Discharge of mine waters into surface waters of the Odra and Vistula river basins in the Slaskie voivodeship – characteristics of the state and forecasts), Dokumentacja nr 42207441-344, GIG, Katowice (in Polish).

Martinez-Carballo E., Gonzalez-Barreiro C., Sitka A., Kreuzinger N., Scharf S., Gans O., 2007, Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria, Environ. Pollut.146(2): 543–547.

McDonell G., Russel A.D., 1999, Antiseptics and disinfectants: activity, action and resistance, Clin. Microbiol. Rev. 12(1): 147–179.

Myers D., 2005, Surfactant science and technology, Wiley-Interscience, New Jersey, 380 pp.

Namieśnik J. (ed.), 1992, Metody instrumentalne w kontroli zanieczyszczeń środowiska (Instrumental methods for controlling environmental pollution), Wydaw. PGdań., Gdańsk, 407 pp (in Polish).

Nelson R.C., 1982, Application of surfactants in the petroleum industry, J. Am. Oil Chem. Soc. 59(10): 823A–826A.

Nocoń W., Kostecki M., Kozłowski J., 2006, Charakterystyka hydrochemiczna rzeki Kłodnicy (Hydrochemistry of the Kłodnica River), Ochr. Śr. 28(3): 39–44 (in Polish).

Nomura Y., Ikebukuro K., Yokoyama K., Takeuchi T., Arikawa Y., Ohno S., Karube I., 1998, Application of a linear alkylbenzene sulfonate biosensor to river water monitoring, Biosens. Bioelectron. 13(9): 1047–1053.

[OECD] Organisation for Economic Cooperation and Development, 2000, Linear Alkylbenzene Sulfonate (LAS) Organization for Economic Cooperation and Development (OECD) Screening Information Data Set (SIDS) Initial Assessment Report for 20th SIDS International Assessment Meeting (SIAM), The CLER Review 10(1): 1–104.

Ogonowski J., Tomaszkiewicz-Potępa A., 1999, Związki powierzchniowo czynne (Surfactants), Wydaw. PKrak., Kraków, 159 pp (in Polish).

Olkowska E., Polkowska Ż., Namieśnik J., 2011, Analytics of surfactants in the environment: Problems and challenges, Chem. Rev. 111(9): 5667–5700.

Olkowska E., Polkowska Ż., Namieśnik J., 2012, Analytical procedures for the determination of surfactants in environmental samples, Talanta 88: 1–13.

Olkowska E., Polkowska Ż., Namieśnik J., 2013, A solid phase extraction–ion chromatography with conductivity detection procedure for determining cationic surfactants in surface water samples, Talanta 116: 210–216.

Olkowska E., Ruman M., Polkowska Ż., 2014, Occurrence of surface active agents in the environment, J. Anal. Methods Chem., Article ID 769708, 15 pp.

Petrovic M., Fernández-Alba A.R., Borrull F., Marce R.M., González M.E., Barceló D., 2002, Occurrence and distribution of nonionic surfactants, their degradation products, and linear alkylbenzene sulfonates in coastal waters and sediments in Spain, Environ. Toxicol. Chem. 21(1): 37–46.

Plaza S., Margielewski L., 2009, Surfactants Lubricating Oil Additives, [in:] Luo J., Meng Y., Shao T., Zhao Q. (eds), Advanced Tribology, Springer, Berlin-Heidelberg: 920–921.

Rapaport R.A., Eckhoff W.S., 1990. Monitoring linear alkylbenzene sulfonate in the environment: 1973-1986, Environ. Toxicol. Chem. 9(10): 1245–1257.

Sablayrolles C., Montréjaud-Vignoles M., Silvestre J., Treilhou M., 2009, Trace Determination of Linear Alkylbenzene Sulfonates: Application in Artificially Polluted Soil – Carrots System, Inter. J. Anal. Chem., Article ID 404836, 6 pp.

Schramm L.L., Stasiuk E.N., Marangoni D.G., 2003, Surfactants and their applications, Annu. Rep. Prog. Chem., Sect. C Phys. Chem. 99: 3–48.

Sekhon B.S., 2013, Surfactants: Pharmaceutical and medicinal aspects, J. Pharm. Technol. Res. Manage. 1: 11–36.

Staszewski R. (ed.), 1990, Kontrola chemicznych zanieczyszczeń środowiska. Podstawy teoretyczne z ćwiczeniami laboratoryjnymi (Control of the chemical pollution of the environment. Theoretical basics with laboratory exercises), Wydaw. PG., Gdańsk, 214 pp (in Polish).

Strugała-Wilczek A., Bebek M., Rodak A, 2013, Ocena przydatności ciągłej analizy przepływowej do badania anionowych i niejonowych substancji powierzchniowo czynnych w próbkach wód i ścieków (Evaluation of the usefulness of continuous flow analysis for the study of anionic surfactants and nonionic surfactants in water and sewage samples), Inż. Ekolog. 32: 172–180 (in Polish, English summary).

Sun H. F., Takata A., Hata N., Kasahara I., Taguchi S., 2003, Transportation and fate of cationic surfactant in river water, J. Environ. Monitor. 5(6): 891–895.

Tabor C.F., Barber L.B., 1996, Fate of linear alkylbenzene sulfonate in the Mississippi River, Environ. Sci. Technol. 30: 161–171.

Traverso-Soto J.M., González-Mazo E., Lara-Martín P.A, 2012, Analysis of surfactants in environmental samples by chromatographic techniques, [in:] de Azevedo Calderon L. (ed.), Chromatography – The most versatile method of chemical analysis, InTech, Rijeka: 187–216.

Trochim M., 2006, Przekształcenie rzeźby terenu i stosunków wodnych na obszarze zlewni Kłodnicy (The transformation of the terrain and water conditions in the Kłodnica catchment), [in:] Machowski R., Ruman M. (eds) Z badań nad wpływem antropopresji na środowisko. T. 7 (Research on the impact of antropopression on the environment. Vol. 7), Wydaw. WNoZ UŚ, Sosnowiec: 151–161.

Utsunomiya A., Watanuki T., Matsushita K., Tomita I., 1997, Toxic effects of linear alkylbenzene sulfonate, quaternary alkylammonium chloride and their complexes on *Dunaliella* sp. and *Chlorella pyrenoidosa*, Environ. Toxicol. Chem. 16(6): 1247–1254.

Ying G.G., 2006, Fate, behavior and effects of surfactants and their degradation products in the environment, Environ. Inter. 32(3): 417–431.

Zieliński R., 2009, Surfaktanty. Budowa, właściwości, zastosowania (Surfactants. Structure, properties, applications), Wydaw. Uniwersytetu Ekonomicznego w Poznaniu, Poznań, 651 pp (in Polish).