

# Surfactants: a real threat to the aquatic geoecosystems of lobelia lakes

Maciej Markowski<sup>1\*</sup>, Włodzimierz Golus<sup>1</sup>, Żaneta Polkowska<sup>2</sup>, Monika Kwidzińska<sup>1</sup>

<sup>1</sup>Department of Limnology, Faculty of Oceanography and Geography, University of Gdańsk, Bażyńskiego 4, 80-309 Gdańsk, Poland, e-mail: geomma@ug.edu.pl (\*corresponding author), geowg@ug.edu.pl, monika.kwidzinska@onet.eu

<sup>2</sup>Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland, e-mail: zanpolko@pg.gda.pl

**Abstract:** Lobelia lakes are valuable elements of the natural environment. They are characterised by low trophic, mainly in-forest location and a high transparency of water. However, similarly to other surface waters, they are subjected to increasing anthropogenic pressures, a good indicator of which is the level of surfactants, also called surface-active agents (SAAs). The aim of the study was to evaluate the intensity of anthropogenic pressures in 13 selected lobelia lakes and 14 streams in the catchments of these lakes in Northern Poland, based on SAA concentrations in the waters of these water bodies. We collected one water sample from each of these water bodies and determined the concentrations of cationic, anionic and non-ionic SAAs. We then compared the results with data concerning the ways in which these catchments and water bodies are used. While ionic (cationic and anionic) SAAs were found to be present in all the 27 samples (with concentrations ranging from 0.05 to 0.51 mg dm<sup>-3</sup>), non-ionic SAAs were identified in 17 of 27 samples (from 0.00 to 2.43 mg dm<sup>-3</sup>) with three samples largely exceeding the maximum concentration values reported by other authors. We concluded that SAAs are a real threat to the aquatic geoecosystems of lobelia lakes and that the pressures of tourism and leisure have the greatest impact.

**Key words:** lobelia lakes, surfactants, surface-active substances, anthropogenic pressure

## Introduction

The natural environment is a complex but very well functioning system in the absence of anthropogenic pressures. However, increasing anthropogenic pressures interfere with its functioning and lead to degradation of its individual components. This system is made up by objects between which certain interrelations may be identified that result from the flow of energy and circulation of matter. In landscape geoecology, such systems are referred to as geoecosystems (Kostrzewski 1991, 1993). Geoecosystems that are both particularly endangered by and susceptible to degradation are lakes. Lakes play the role of water bodies that retain matter, while their feeding streams serve as a source of energy and matter for these hydrographic objects. Thus the geoecosystem of a lake is not only made up by the very water body (the lake) but also by its catchment. The functioning of individual lake geoecosystems is determined by a number of factors that principally include climatic factors, hydrological factors, environmental features of the catchment and the limnologic features of the water body (Markowski and Kwidzińska 2015). However, the func-

tioning of a lake geoecosystem is mainly based on the constant transport of matter from the catchment and on the accumulation of matter within the lake. Matter is supplied to the lake from two sources: surface sources (via transport from the catchment) and point sources (i.e. the feeding streams). Previous papers on the functioning of lake geoecosystems have pointed to streams as the main source of pollution. Along with stream water, lakes are supplied with a number of substances responsible for lake degradation, with biogenic substances, such as nitrogen and phosphorus compounds being among the most commonly listed ones. Obviously, these are not the only compounds responsible for lake degradation. With the progress of human civilisation, increasingly complex chemical compounds are introduced to the aquatic environment, such as hydrocarbons, pharmaceuticals (which include antibiotics and hormones), pesticides, herbicides, phenols and many others. Their presence affects and changes the aquatic environment, and due to the limited possibilities of researchers investigating the pollution of inland waters, these substances are often omitted in basic water quality tests. Surfactants belong to a group of compounds that are

frequently used by humans in every aspect of their activity and are often omitted when evaluating the degree of water degradation.

### Surfactants

Surfactants comprise the various chemical compounds referred to as surface-active agents (SAAs) that have been used by humans for centuries. Initially, these were substances of natural origin for the production of which such plants as chestnuts, walnuts or lemons were used. Currently, synthetic substances are used for their production. Surfactants are not only widely used in households but also in industry. Thanks to their amphophilic properties, surfactants have been used as washing substances, softeners, wetting agents, foaming agents, thickeners and emulsifiers, semiconductors, and materials for the manufacture of paints and varnishes (Ying 2006; Myers 2005). They are commonly used in households and are found in washing and cleaning agents, medicines, antibacterial and antifungal agents, cosmetics, paints, petroleum products and even in foods. Thanks to a wide spectrum of applications, the annual production volume of surfactants ranges, depending on the source, from 15 to 18 million tonnes (Lara-Martin et al. 2006). After they have been utilised, most surfactants, along with waste water, reach water treatment plants, where they are subjected to degradation processes. This way pretreated waters are emitted to surface waters, where they undergo deposition in sediments or are assimilated by living organisms and accumulated in their tissues (Olkowska et al. 2015). Scientists have voiced opinions according to which the very process of surfactant degradation can result in the formation of new, even more toxic compounds (Olkowska et al. 2017). The widespread access to SAAs and the progressive anthropogenic pressures on aquatic geoecosystems pose a real risk of direct pollution of surface and ground waters with surfactants. The presence of surfactants in the aquatic environment is important in that the natural properties of these substances allow them to penetrate to atmospheric air (Olkowska et al. 2011). Along the moving air masses SAAs may be transported over long distances, and together with dry or wet deposition, they enter waters and soils, where they are taken up by living organisms (Fries and Puttmann 2004). The presence of surfactants in water may not only have an unfavourable effect on the living functions of aquatic organisms but also on those of humans. SAAs are toxic to living organisms. They have been proved to exert adverse effects, such as endocrine disorders, skin irritation, and can also trigger allergies (Olkowska et al. 2011). They also facilitate the dissolution of many toxins dangerous to aquatic organisms, including pesticides. In lake ecosystems, the

presence of surfactants may markedly accelerate the process of water eutrophication by restricting oxygen diffusion to the deeper parts of the water body as a result of surfactant adsorption on the water surface. The presence of surfactants is an indicator of the progressive degradation of surface waters (Olkowska et al. 2013a). Their presence at higher concentrations can easily be identified when foam is observed to form on the surface during the mixing of water. Detection of individual SAAs in water is now, however, relatively simple and requires appropriate sample preparation, as extensively discussed by Olkowska et al. (e.g. 2011, 2013a).

Surfactant molecules have a specific chemical structure. Each surfactant is characterised by the presence of two parts: the lyophilic moiety and the lyophobic moiety. In cases of water-soluble SAAs, the former is of a polar/hydrophilic nature and is comprised of an acidic radical or basic residue, while the latter is non-polar/hydrophobic and is comprised of simple, branched or aromatic hydrocarbons (Olkowska et al. 2010). In terms of chemical structure, surfactants may be divided into ionic and non-ionic ones. Ionic SAAs fall into anionic, cationic and amphoteric SAAs. The chemical structure of surfactants alone determines their impact on individual elements of the abiotic and biotic environment (Olkowska et al. 2010).

Studies investigating the presence of surfactants in the aquatic environment are mainly limited to those by Olkowska et al. (2010, 2011, 2017). These are mainly methodological studies and only to a small extent reveal the impact of surfactants on the functioning of aquatic geoecosystems. A number of studies have investigated SAA toxicity in living organisms, including aquatic organisms, such as the algae or the *Daphnia* species (Olkowska et al. 2013a, b, c). SAA concentrations in surface waters are usually in the range from 0.0 to more than 2 mg dm<sup>-3</sup> (Table 1). The allowable non-chargeable quantity of surfactants in water released by the water treatment plant in Gdańsk, Poland, into surface waters is several times higher than the SAA concentrations noted in surface waters (Table 1).

The available literature data on SAA concentrations in surface waters are very limited. They usually concern only several substances (e.g. DDT or herbicides) or provide detailed information on SAA accumulation in aquatic organisms. According to some authors (Muramoto et al. 1996; Ivanković and Hrenović 2010; Ghose

Table 1. Surfactant concentrations in surface waters (Olkowska 2011) and the SAA contamination levels allowed by Saur Neptun Gdańsk in waste water (SNG 2017). Values are given in mg dm<sup>-3</sup>

| C-SURF     | A-SURF     | N-SURF      | References      |
|------------|------------|-------------|-----------------|
| 0.0 to 0.4 | 0.0 to 0.2 | 0.0 to >2.0 | Olkowska (2011) |
| No data    | 15.0       | 20.0        | SNG (2017)      |



et al. 2009), SAA concentration values acceptable in surface waters should not exceed  $1 \text{ mg dm}^{-3}$ .

Given the considerable ability of SAAs to migrate, contamination with these compounds is observed in all the surface waters in Poland. It is present in all the geoecosystems, including those that are most valuable in terms of nature-related aspects and protected by law, with lobelia lakes being one such category.

### Lobelia lakes

Lobelia lakes are water bodies in which certain characteristic plant species called isoetids are found together or separately. These plants are: water lobelia, also called Dortmann's cardinalflower (*Lobelia dortmanna*), lake quillwort, also called Merlin's grass (*Isoetes lacustris*), spiny quillwort, also called spiny-spored quillwort or spring quillwort (*Isoetes echinospora*), and *Littorella uniflora*. The following are often typical of lobelia lakes but are also found in other water types: alternate-flowered water-milfoil (*Myriophyllum alterniflorum*), and, less frequently, floating water-plantain (*Luronium natans*), and narrow-leaved bur-reed (*Sparganium angustifolium*) (e.g. Wilk-Woźniak et al. 2012; Szmidt and Bociąg 2017). A total of 173 water bodies have been identified in Poland whose flora includes at least one species of isoetids (Szmidt and Bociąg 2017). Lobelia lakes are valuable and rare aquatic geoecosystems. All the species of isoetids are plants protected by law, and the lakes where they are found are often included in the Nature 2000 network.

Lobelia lakes are interesting examples of lakes characterised by low trophic state and soft water with low calcium content. In addition to the presence of indicator species, the characteristic features of these water bodies include high transparency of water, presence of a watershed in the vicinity, and often a beautiful and attractive location. Although, generally, these lakes are found throughout Poland, the vast majority are located in Pomerania, where a total of 171 have been identified (accounting for 99% of their total number in Poland). The extraordinary and valuable geoecosystems of lobelia lakes, just like those of all the other lakes in Poland, are being subjected to increasing anthropogenic pressures. Disappearance of indicator species that form assemblages in lobelia lakes and progressive eutrophication of these

lakes is being observed. Due to their exceptional nature, the geoecosystems of these lakes generate increasing interest among researchers, who are concerned about the growing number of degraded lobelia lakes (Kraska 1994a, b; Kraska et al. 2013). There are intensifying efforts to determine ways to save these unique elements of the Polish lake districts landscape. Numerous studies are being carried out to assess the level of risk to the aquatic environment based on analyses of the chemical composition of lobelia lake waters, although none of them have yet considered surfactants. We therefore set out to perform the first quantitative and qualitative identification of surfactants in the waters of lobelia lakes and in their feeding streams. We evaluated three classes of surfactants: cationic, anionic and non-ionic, taking into account the structure of catchment uses, ways of using the lake shoreline and the water body, and morphometric features of the lakes as elements having the greatest effect on SAA quantities in the water of natural water bodies.

### Study area and methods

We selected 13 lobelia lakes along with the streams found within their catchments located closest to the Tricity (Gdańsk, Sopot, Gdynia) agglomeration. These were catchments of the following lakes: Karlikowskie (Karlikowo), Sitno, Głębokie, Techlinko (Techlinka), Otałżyno, Wysokie (Wycztok), Jelonek, Brzeżonko, Kamień, Borowo, Bieszkowickie, Zawiat, and Osowskie (Fig. 1 and Table 2). The catchments of these lakes are located within the Kashubian Lakeland and are situated in a moraine landscape. They belong to three river basins: Radunia (Karlikowskie, Sitno, Głębokie, Techlinko, Osowskie), Reda (Otałżyno, Jelonek, Wysokie, Brzeżonko, Kamień, Borowo), and Zagórska Struga (Bieszkowickie, Zawiat).

Due to the periodic nature of the river network of the lobelia lake catchments located on moraine plateaus (Markowski and Kwidzińska 2015) we decided to carry out water sampling for the purposes of measuring the concentrations of surfactants during the period of the highest catchment retention, when the river network of these areas is best developed (Bajkiewicz-Grabowska and Golus 2009). We therefore selected the period of

Table 2. Geoecosystems and symbols used to identify watercourses

| Geoecosystem (Lake) | Stream's symbol    | Geoecosystem (Lake) | Stream's symbol |
|---------------------|--------------------|---------------------|-----------------|
| Karlikowskie        | –                  | Brzeżonko           | Br1             |
| Sitno               | Si1, Si2, Si3      | Kamień              | Ka1, Ka2        |
| Głębokie            | –                  | Borowo              | –               |
| Techlinko           | –                  | Bieszkowickie       | –               |
| Otałżyno            | Ot1, Ot2, Ot3, Ot4 | Zawiat              | –               |
| Wysokie             | Wy1, Wy2, Wy3, Wy4 | Osowskie            | –               |
| Jelonek             | –                  |                     |                 |



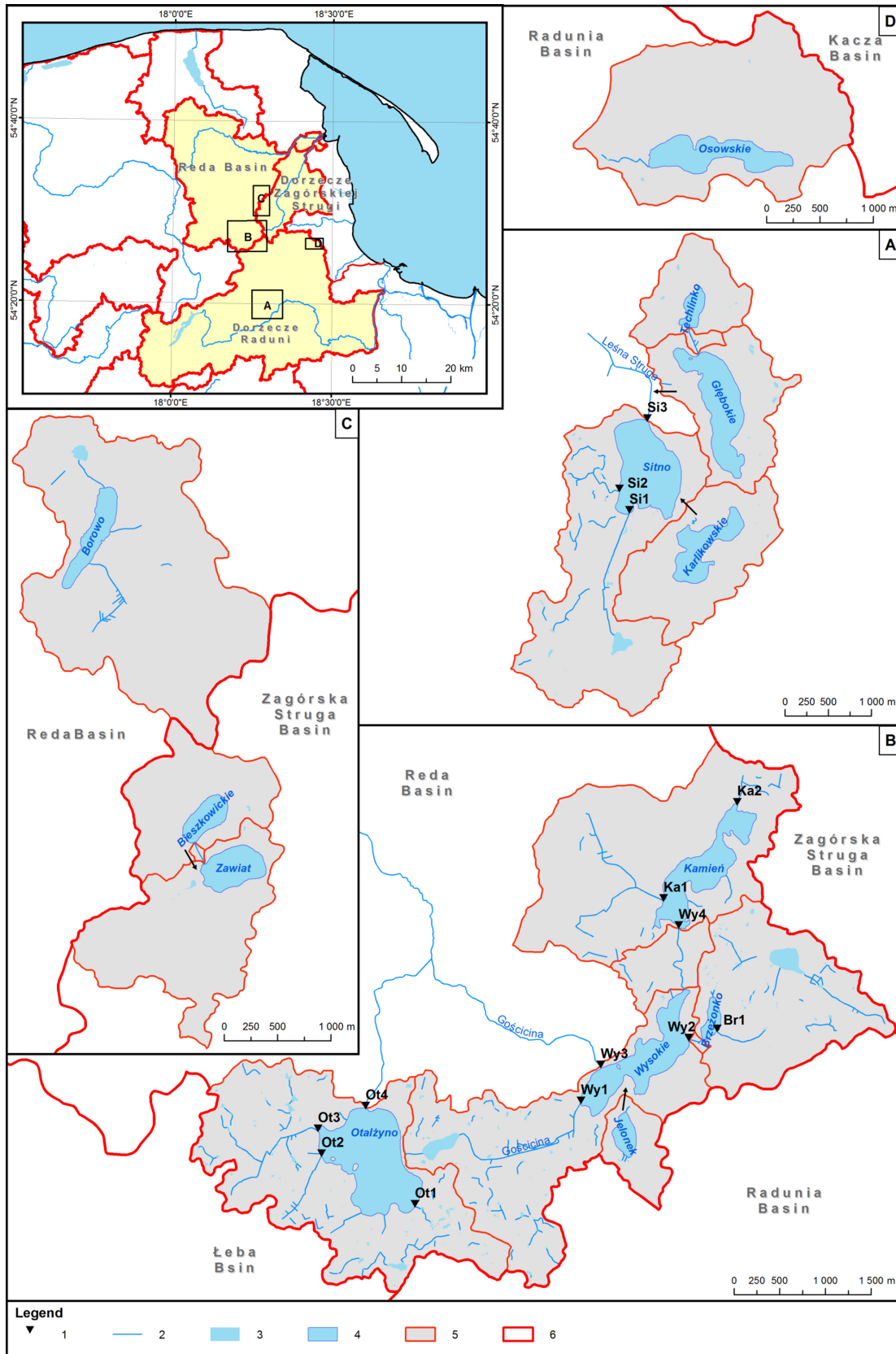


Fig. 1. Studied geocosystems

Explanation: 1 – sampling points; 2 – streams; 3 – other water bodies; 4 – studied lakes; 5 – studied catchments; 6 – other catchments

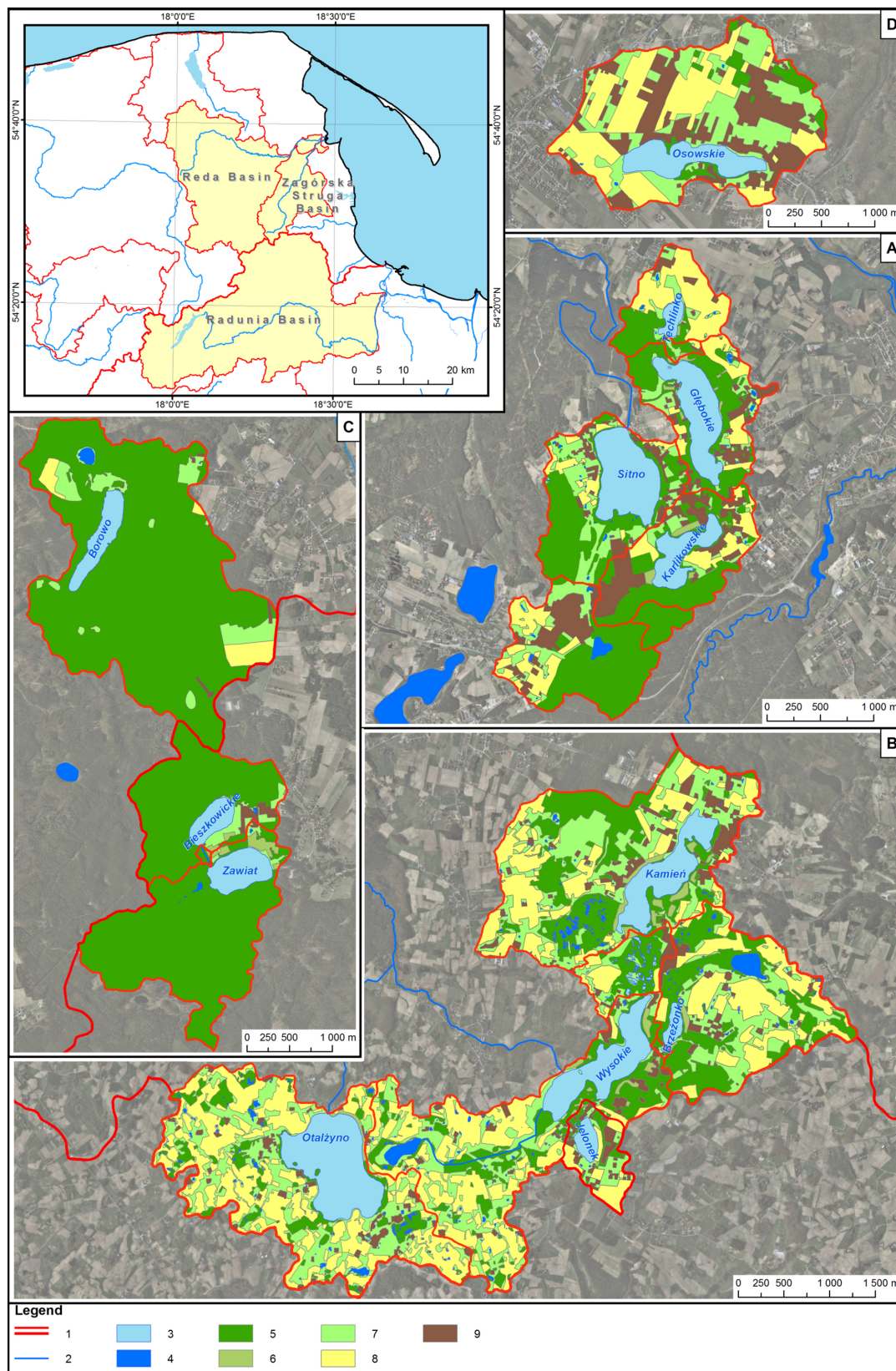


Fig. 2. The uses of the catchments of the selected lobelia lake geocoecosystems

Explanation: 1 – watersheds; 2 – streams; 3 – lobelia lakes included in the study; 4 – the other water bodies; 5 – forests; 6 – a forest with summer houses; 7 – green areas (meadows, pastures, fallow lands); 8 – agricultural areas; 9 – built-up areas

early spring 2010, when a maximum catchment retention was noted and the highest density of the river network was observed in the catchments of the lobelia lakes being studied.

The water balance type of the lobelia lakes was determined on the basis of several years of observation and hydrological measurements (2008–2010) of the lakes and the inflowing and outflowing streams. Based on monthly hydrographic mapping of the catchments we determined the lengths of the periods of active inflow and outflow for these lakes. Based on the above we found that one lake (Wysokie) was a flow-through water body and five lakes (Sitno, Techlinko, Otałzyno, Brzeżonko, and Kamień) were lotic water bodies. The remaining seven were endorheic water bodies.

Based on the most recent orthophotomap we identified the most favourable catchment conditions, in terms of the structure of direct catchment uses, to be present in the catchments of the following lakes: Borowo, Zawiat, and Bieszkowickie. The feeding area for these lakes is located within the Darżlubie Forest (*Puszcza Darżłubska*) and forests account for more than 80% in the structure of use for these catchments (Fig. 2). The catchments of the following lakes are characterised by particularly unfavourable conditions of use: Karlikowskie, Sitno, and Lake Osowskie. These catchments are characterised by a high percentage of agricultural areas (Fig. 2) with a considerable percentage of built-up areas (Markowski and Kwidzińska 2015).

Laboratory analyses were carried at the Laboratory of the Faculty of Chemistry, Gdansk University of Technology, and included the sum of ionic (anionic and cationic) and non-ionic surfactants. Appropriate methods of measurement are an essential tool when examining SAAs in environmental samples. The greatest challenges to the chemist are posed by the complex composition of the samples, the low levels of individual analytes and the amphiphilic properties of the analytes. In order to eliminate these difficulties we used appropriate extraction techniques at the sample preparation stage, followed by SAA identification and quantitation. The samples were prepared for analysis using the SPE or ASE/UAE-SPE techniques and the analytes were identified and quantitated using ion chromatography (with CD or UV detection) or two-dimensional gas chromatography combined with mass spectrometry (GCxGC/MS). We compared the effectiveness of analyte isolation from the environmental samples during the preparation of appropriate solvent extracts using the above techniques. We determined the basic validation parameters for these analytical procedures. The methods used for the evaluation of surfactant concentrations in water and the issues surrounding their determination are extensively discussed in the literature and are not within the scope of this paper.

## Results

The laboratory analysis of the water samples collected from the lakes and streams revealed marked variation in the concentrations of individual SAAs. Most of the lobelia lake geoecosystems were found to be environments where SAAs were present in low concentrations (Fig. 3 and Table 3). The total concentration of surfactants in the water from the investigated geoecosystems ranged from 0.24 to 2.68 mg dm<sup>-3</sup>. The mean total SAA concentration was 0.75 mg dm<sup>-3</sup>. The average concentrations of SAAs in the samples ranged from 0.42 to 0.72 mg dm<sup>-3</sup>. The lowest SAA concentrations were observed in stream Si3 and Lakes Techlinko and Osowskie, namely less than 0.32 mg dm<sup>-3</sup>. The highest sums of all surfactant classes were found in tributary Ot2 of Lake Otałzyno (2.86 mg dm<sup>-3</sup>) and in stream Wy4 (2.36 mg dm<sup>-3</sup>) within the Lake Wysokie system. This lake also revealed high concentrations at 2.30 mg dm<sup>-3</sup>, which exceeds the norms for surface waters. Seventy-five percent of lobelia lake geoecosystems in the Tricity area had SAA concentrations below the arithmetic mean, which indicates a wide range of SAA concentrations, although the values are generally low. A similar distribution was observed for the concentrations of the individual surfactant classes (cationic, anionic and non-ionic SAAs).

Concentrations of cationic SAAs (C-SURF) in the water from the selected lobelia lake geoecosystems ranged from 0.06 mg dm<sup>-3</sup> in Lake Borowo to 0.51 mg dm<sup>-3</sup> in Lake Kamień. They were therefore within or slightly exceeded the C-SURF concentration ranges noted in surface waters (Table 1). C-SURF concentra-

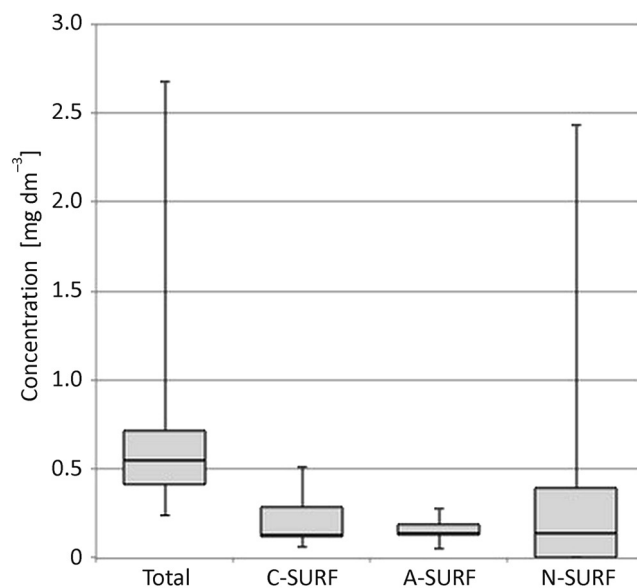


Fig. 3. Minimum, maximum and interquartile range of total, cationic (C-SURF), anionic (A-SURF) and non-ionic (N-SURF) SAA concentrations in the water samples collected during the study



Table 3. Concentration of surfactants in water samples. Values are given in  $\text{mg dm}^{-3}$ 

| Sample        | Surface active agents |         |           | Total |
|---------------|-----------------------|---------|-----------|-------|
|               | Cationic              | Anionic | Non-ionic |       |
| Karlikowskie  | 0.12                  | 0.14    | 0.39      | 0.65  |
| Sitno         | 0.28                  | 0.06    | 0.10      | 0.44  |
| Si1           | 0.12                  | 0.13    | 0.28      | 0.53  |
| Si2           | 0.28                  | 0.13    | 0.00      | 0.41  |
| Si3           | 0.13                  | 0.11    | 0.00      | 0.24  |
| Głębokie      | 0.29                  | 0.14    | 0.00      | 0.43  |
| Techlinko     | 0.13                  | 0.13    | 0.00      | 0.26  |
| Otalżyno      | 0.12                  | 0.11    | 0.10      | 0.33  |
| Ot1           | 0.13                  | 0.18    | 0.11      | 0.42  |
| Ot2           | 0.12                  | 0.13    | 2.43      | 2.68  |
| Ot3           | 0.09                  | 0.17    | 0.00      | 0.26  |
| Ot4           | 0.13                  | 0.11    | 0.56      | 0.80  |
| Jelonek       | 0.24                  | 0.20    | 0.00      | 0.44  |
| Wysokie       | 0.08                  | 0.18    | 2.04      | 2.30  |
| Wy1           | 0.46                  | 0.22    | 0.00      | 0.68  |
| Wy2           | 0.29                  | 0.15    | 0.36      | 0.80  |
| Wy3           | 0.32                  | 0.16    | 0.10      | 0.58  |
| Wy4           | 0.22                  | 0.16    | 1.98      | 2.36  |
| Brzeżonko     | 0.30                  | 0.21    | 0.18      | 0.69  |
| Br1           | 0.21                  | 0.28    | 0.00      | 0.49  |
| Kamień        | 0.51                  | 0.13    | 0.57      | 1.21  |
| Ka1           | 0.13                  | 0.28    | 0.00      | 0.41  |
| Ka2           | 0.32                  | 0.25    | 0.39      | 0.96  |
| Borowo        | 0.06                  | 0.10    | 0.45      | 0.61  |
| Bieszkowickie | 0.25                  | 0.13    | 0.27      | 0.65  |
| Zawiat        | 0.11                  | 0.05    | 0.30      | 0.46  |
| Osowskie      | 0.12                  | 0.20    | 0.00      | 0.32  |
| Minimum       | 0.06                  | 0.05    | 0.00      | 0.24  |
| Mean          | 0.21                  | 0.16    | 0.39      | 0.76  |
| Maximum       | 0.51                  | 0.28    | 2.43      | 2.68  |

tions in 50% of the water samples were below the arithmetic mean of  $0.21 \text{ mg dm}^{-3}$ . The highest concentrations of cationic SAAs exceeded  $0.2 \text{ mg dm}^{-3}$  and were observed in Lake Wysokie tributaries. In addition to

Lake Borowo, low levels of C-SURF were also identified in Lake Zawiat and Lake Otalżyno.

The smallest variations in SAA concentrations were observed in the case of anionic surfactants (A-SURF). A-SURF were present in all the samples and their concentrations ranged from  $0.05 \text{ mg dm}^{-3}$  in Lake Zawiat to  $0.28 \text{ mg dm}^{-3}$  in Ka1. The mean concentration of anionic SAAs in the water was  $0.16 \text{ mg dm}^{-3}$ . A-SURF concentrations were within or slightly exceeded the range observed for surface waters (Table 1). Low concentrations of A-SURF were also measured in Lakes Sitno ( $0.06 \text{ mg dm}^{-3}$ ) and Borowo ( $0.10 \text{ mg dm}^{-3}$ ). High concentrations of A-SURF (above  $0.20 \text{ mg dm}^{-3}$ ) were measured in Lakes Brzeżonko, Jelonek and Osowskie, and in the tributaries of Lake Kamień. In 50% of the water samples, the concentrations of A-SURF ranged from  $0.13$  to  $0.17 \text{ mg dm}^{-3}$ .

The greatest variations in SAA concentrations in the water of lobelia lake geocosystems in the Tricity area were observed in the case of non-ionic SAAs. No N-SURF were identified in as many as 10 samples, while in two samples (Lakes Otalżyno and Sitno), the concentrations of N-SURF were below the level of detection ( $<0.1 \text{ mg dm}^{-3}$ ). The mean N-SURF concentration of the investigated geocosystems was  $0.39 \text{ mg dm}^{-3}$ . The highest N-SURF concentrations exceeded  $2 \text{ mg dm}^{-3}$  and were measured in Lake Wysokie ( $2.30 \text{ mg dm}^{-3}$ ), in the Wy4 ( $2.36 \text{ mg dm}^{-3}$ ) and Ot2 ( $2.68 \text{ mg dm}^{-3}$ ) streams. In 75% of the samples, N-SURF concentrations did not exceed the mean N-SURF value. The N-SURF concentrations of the investigated geocosystems were typical for surface waters (Table 1).

The concentrations of cationic surfactants (C-SURF) assumed a distribution similar to the left-skewed asymmetric distribution (Fig. 4), which indicates generally low C-SURF concentrations in the water samples. The distribution of individual concentrations of A-SURF

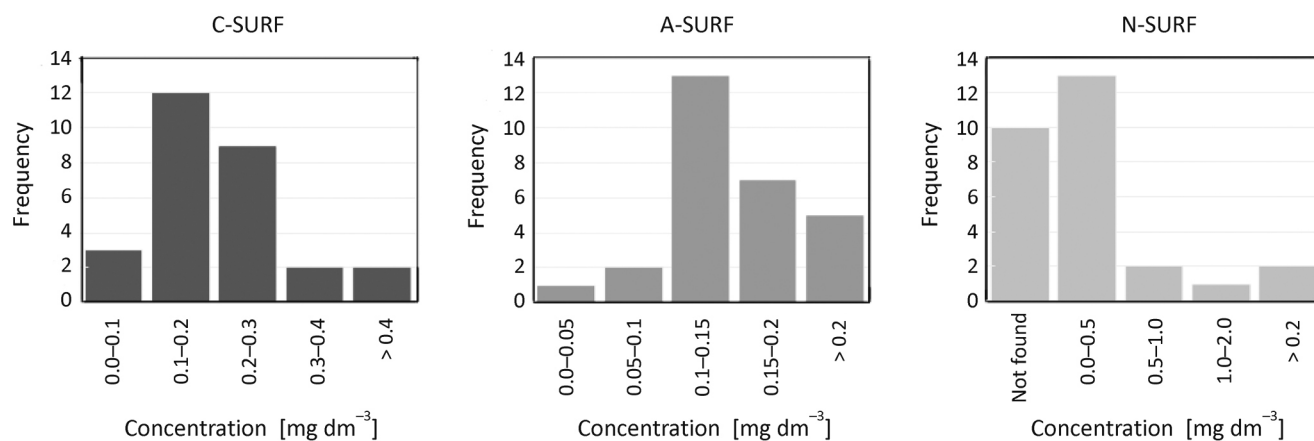


Fig. 4. Frequency distribution of surfactant concentrations in water samples within cationic (C-SURF), anionic (A-SURF) and non-ionic (N-SURF) classes of surfactants

was that of a right-skewed distribution (Fig. 4) with the highest number of medium and high concentration values. The concentrations of non-ionic surfactants in the samples assumed a bimodal asymmetric distribution with features of a right-skewed distribution (Fig. 4), indicating a heterogenous population of the lobelia lake geoecosystems in terms of N-SURF presence in their waters. Low concentrations of N-SURF or absence of N-SURF were most commonly observed in samples. On the other hand, in those geoecosystems whose waters revealed the presence of N-SURF, the N-SURF concentrations were generally high.

The distribution of the individual SAA classes in the waters of the Tricity lobelia lake geoecosystems revealed a large variation of these elements of the natural environment in terms of the observed SAA concentrations. Most of the geoecosystems were characterised by the presence of SAAs in the water in concentrations that did not exceed  $0.4 \text{ mg dm}^{-3}$  (Fig. 5). The smallest fluctuations of concentration were noted for A-SURF. The fluctuations of C-SURF concentrations were also small. The greatest variation was noted for the concentrations of N-SURF, whose presence caused some of the geoecosystems to fall outside the scale adopted for SAA concentrations.

The contribution of the individual classes of SAAs in the water of lobelia lake geoecosystems in the Tricity

area shows that these systems may be divided into the following four groups:

1. Geoecosystems where  $A\text{-SURF} > C\text{-SURF}$ , and  $N\text{-SURF} = 0$ . This group includes the geoecosystems of Lake Osowskie, Lake Jelonek, and streams Ka1, Ot3 and Br1.
2. Geoecosystems where  $C\text{-SURF} > A\text{-SURF}$ , and  $N\text{-SURF} = 0$ . This group includes the geoecosystems of Lake Głębokie, Lake Techlinko, and streams Si2, Si3 and Wy1.
3. Geoecosystems where  $N\text{-SURF} < A\text{-SURF} + C\text{-SURF}$ . This group includes the geoecosystems of the following lakes: Sitno, Otałzyno, Brzeżonko, Kamień, and Bieszkowickie, and of the following streams: Si1, Ot1, Wy2, Wy3 and Ka2.
4. Geoecosystems where  $N\text{-SURF} > C\text{-SURF} + A\text{-SURF}$ . This group includes the geoecosystems of the following lakes: Karlikowskie, Borowo and Zawiat, and the following streams: Ot2, Ot4 and Wy4.

## Discussion

Lobelia lakes are water bodies frequently regarded as objects characterised by their high purity of water, for which reason they are often used for leisure purposes. The spatial variation in concentrations of individual SAA classes in the waters of the selected lobelia

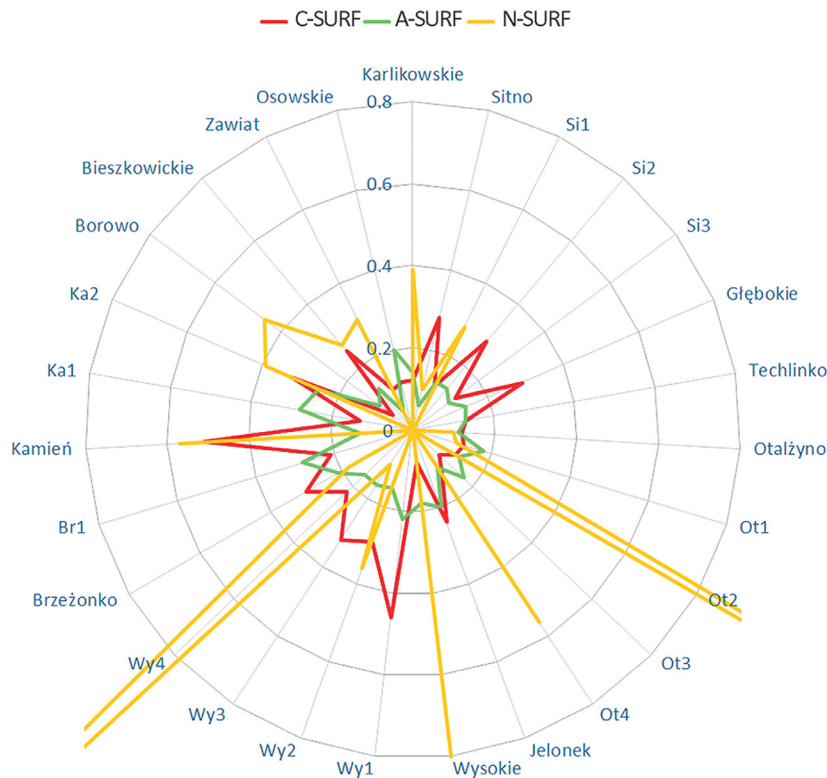


Fig. 5. Distribution of concentrations for the individual surfactant classes at the measurement points



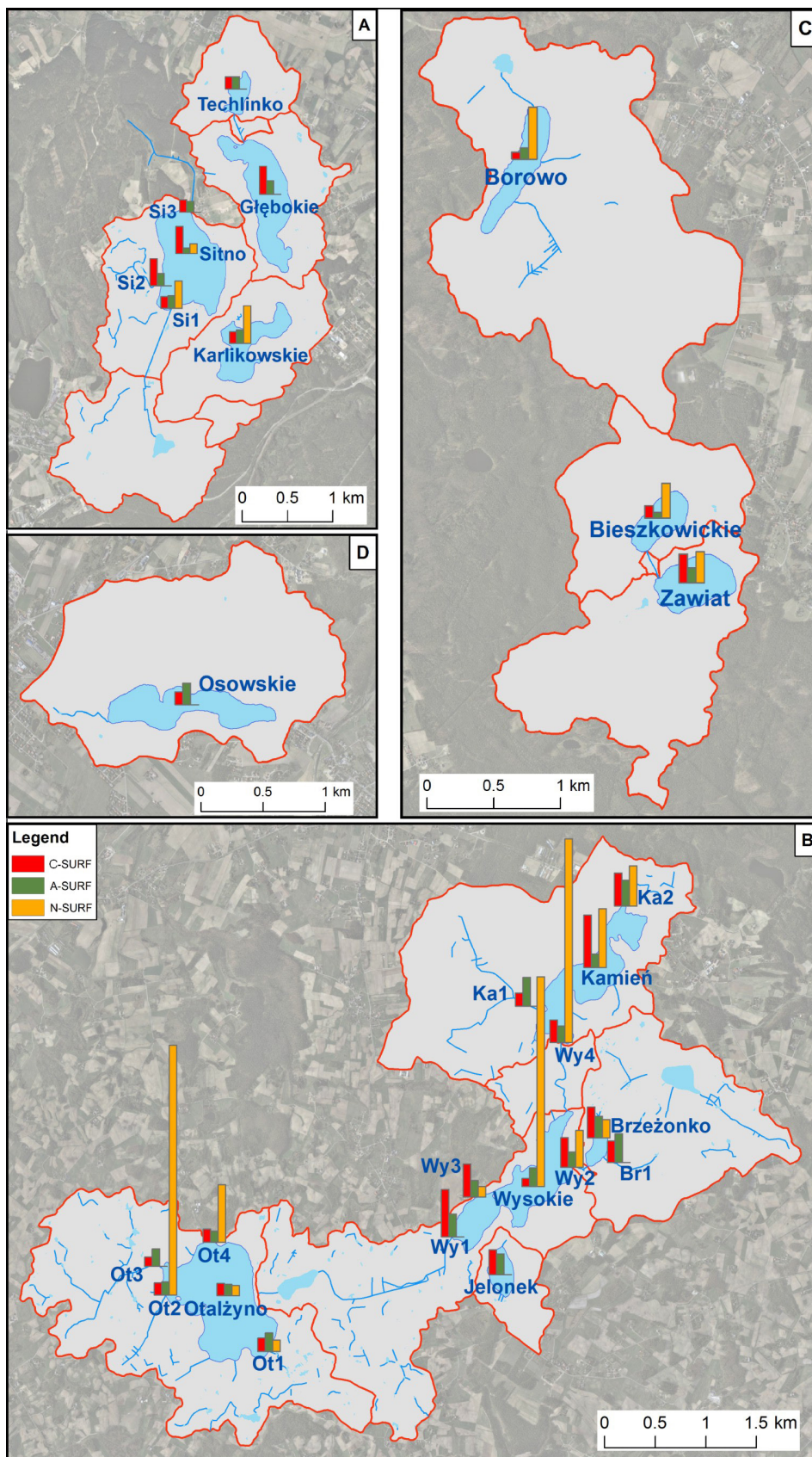


Fig. 6. Spatial variation in surfactant concentrations in studied lobelia lake geocoecosystems within the Tricity area



lake geoecosystems in the Tricity area suggests (Fig. 6) that the direct use of the catchments and the very water bodies are likely to be the most important factor affecting the pollution of their waters with SAAs. The use of these geoecosystems varies greatly, and this is reflected in SAA concentrations and the predominance of specific SAA classes. The clean and forest lakes Borowo, Zawiat and Bieszkowickie are water bodies whose waters should be least contaminated with SAAs. This, however, is not the case. The close proximity of the Tricity agglomeration is to blame here. These water bodies are used as leisure locations by the inhabitants of the entire Tricity. The extremely transparent water of Lake Zawiat coupled with the vast sandy littoral zone have made this lake a place extensively used for leisure purposes. In the summer the lake serves as a swimming complex, which along with the catering facilities in its direct vicinity may serve as a major source of surfactants.

Lake geoecosystems in the areas surrounding the village of Kamień are also used for leisure purposes (Fig. 6B). Allotments with summer houses are situated in the direct vicinity of the following lakes: Wysokie, Jelonek, Brzeżonko, and Kamień. Based on our field studies it may be concluded that the summer houses are also used outside the summer season, which considerably increases the level of anthropogenic pressures on these water bodies. This is evidenced by the relatively high concentrations of C-SURF, which are used in soaps, washing agents and foaming agents. The predominance of C-SURF has also been observed in the case of Lake Kamień and its tributaries, and the geoecosystem of Lake Wysokie – all extensively used by tourists. Lake Wysokie hosts a swimming complex with adjacent small catering and leisure infrastructure typical of large beaches. The unfavourable depth conditions of Lake Kamień facilitate cyanobacteria blooms, which were observed during our field studies (2007–2010).

The geoecosystem of Lake Otałzyno is an interesting example (Fig. 6B). Despite the poor quality of the streams feeding this lake in terms of the concentrations of various SAA classes, the lake waters are characterised by a low SAA concentration. This is most likely due to the shallow depth of this lake, the wide stretch of the plants above and below the water, and the high thickness of the lake bed sediments which can easily take up SAAs from water coming from the inflowing streams (Bajkiewicz-Grabowska et al. 2016). The geoecosystem of Lake Osowskie is another exceptional ecosystem. Although the lake lies within the city limits (in the residential area of Gdańsk-Osowa), the SAA concentrations measured in the water are among the lowest in the investigated geoecosystems. This may be due to the fact that this lake has few places suitable for swimming. Another factor may be that the built-up area located

within the catchment of Lake Osowskie has been connected to the sewage system.

Lobelia lakes are subjected to strong anthropogenic pressures. This is particularly important due to the fact that SAAs reach the lake geoecosystems mainly as a result of human activity. The presence and quantity of surfactants in the waters of lobelia lake geoecosystems is not determined by the way in which the terrain is used but by the intensity of their use as leisure objects. Using lobelia lakes as local swimming complexes seems particularly unfavourable. The situation is made worse by the presence of summer houses, which not only increase the number of people who go for a swim or use the lakes for leisure purposes but are also a source of untreated waste water from houses not connected to the sewage system. The existence of multiple potential sources of contamination of lobelia lake waters with SAAs is evidenced by the fact that a predominance of different surfactant classes is observed in individual geoecosystems. Of particular concern are the high concentrations of non-ionic SAAs in some water bodies, which sometimes reach values noted in untreated waste water (the Lake Kamień geoecosystem).

The increased pressure on lobelia lake geoecosystems has resulted in a deterioration of water quality. Most importantly, however, from the naturalist's point of view, is the disappearance of the rare vascular plants typical of these lakes. As one can see, this is influenced not only by what happens within the catchment, changes of water circulation conditions or the supply of biogenic substances, but also by the presence of substances present in the environment as a direct result of human activity, such as SAAs.

## Conclusion

Analysis of SAA concentrations in the water of lobelia lake geoecosystems in the Tricity area indicates that they are subjected to human anthropogenic pressures. High concentrations (above  $2 \text{ mg dm}^{-3}$ ) of non-ionic SAA or cationic SAA are present in some lakes. The authors assume that the greatest influence on the presence of SAA in lobelia lakes is the direct use of these reservoirs by people for swimming, diving and fishing. Additionally, the presence of summer housing in the vicinity of the lakes is important.

## References

- Bajkiewicz-Grabowska E., Golus W., 2009, Organizacja sieci hydrograficznej w zlewni pojeziernej przy różnym stanie jej retencji (Organisation of river network in a lakeland catchment with different retention status), [in:] Bogdanowicz R., Fac-Beneda J. (eds), *Zasoby i ochrona wód*.



- Obieg wody i materii w zlewniach rzecznych (Water resources and water protection. Water and matter cycling in river basins), FRUG, Gdańsk: 159–166 (in Polish, English summary).
- Bajkiewicz-Grabowska E., Markowski M., Lemańczyk K., 2016, Application of geoinformation techniques to determine zones of sediment resuspension induced by wind waves in lakes (using two lakes from Northern Poland as examples), *Limnol. Rev.* 16(1): 3–16.
- Fries E., Puttmann W., 2004, Occurrence of 4-Nonylphenol in rain and snow, *Atmos. Environ.* 38(13): 2013–2016.
- Ghose N., Saha D., Gupta A., 2009, Synthetic detergents (surfactants) and organochlorine pesticide signatures in surface water and groundwater of Greater Kolkata, India. *J. Water Resour. Prot.* 1(4): 290–298.
- Ivanković T., Hrenović J., 2010, Surfactants in environment, *Arh. Hig. Rada Toksikol.* 61(1): 95–110.
- Kostrzewski A. (ed.), 1991, *Koncepcja programu: Monitoring obiegu materii – kompleksowy monitoring środowiska przyrodniczego w podstawowych typach geoeosystemów Polski* (Conception of the energy and matter cycle monitoring programme: An integrated monitoring of the natural environment in basic types of Poland's geoeosystems), *Kom. Nauk. Prez. PAN "Człowiek i Środowisko"*, Poznań, 112 pp (in Polish).
- Kostrzewski A., 1993, *Geoeosystem obszarów nizinnych. Koncepcja metodologiczna* (The geoeosystem of lowland areas. A methodologica lconception), [in:] Kostrzewski A. (ed.), *Geoeosystem obszarów nizinnych* (The geoeosystem of lowland areas), *Zesz. Nauk. Kom. Nauk. PAN „Człowiek i Środowisko”* 6: 11–17 (in Polish, English summary).
- Kraska M. (ed.), 1994a, *Jeziora lobeliowe. Charakterystyka, funkcjonowanie i ochrona. Część I* (The lobelia lakes. Characteristics, functioning and protection. Part I), *Idee Ekol.* 6(4): 9–177 (in Polish, English summary).
- Kraska M. (ed.), 1994b, *Jeziora lobeliowe. Charakterystyka, funkcjonowanie i ochrona. Część II* (The lobelia lakes. Characteristics, functioning and protection. Part II), *Idee Ekol.* 7(5): 9–105 (in Polish, English summary).
- Kraska M., Klimaszuk P., Piotrowicz R., 2013, Anthropogenic changes in properties of the water and spatial structure of the vegetation of the lobelia lake Lake Modre in the Bytów Lakeland, *Oceanogr. Hydrobiol. Stud.* 42(3): 302–313.
- Lara-Martin P., Gomez-Parra A., Gonzalez-Mazo E., Chromatogr A., 2006, Simultaneous extraction and determination of anionic surfactants in waters and sediments, *J. Chromatogr. A* 1114(2): 205–210.
- Markowski M., Kwidzińska M., 2015, Types of geoeosystems of the lobelia lakes of the Tricity area, *Quaest. Geogr.* 34(1): 15–25.
- Muramoto S., Aoyama I., Hashimoto K., Kungolos A., 1996, Distribution and fate of surface active agents in river and lake water, affected by domestic and agricultural wastewater, in an area in Japan, *J. Environ. Sci. Heal. A* 31(4): 721–729.
- Myers D., 2005, *Surfactant science and technology*, Wiley-Interscience, Hoboken, 380 pp.
- Olkowska E., Polkowska Ż., Namieśnik J., 2010, Występowanie surfaktantów w próbkach środowiskowych (Occurrence of surfactants in the environmental samples), *Wiad. Chem.* 64(9–10): 809–830 (in Polish, English summary).
- 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., 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., Kowalska A., Polkowska Ż., 2013a, Determination of surfactants in environmental samples Part I. Cationic compounds, *Ecol. Chem. Eng. S.* 20(2): 331–342.
- Olkowska E., Ruman M., Kowalska A., Polkowska Ż., 2013b, Determination of surfactants in environmental samples Part II. Anionic compounds, *Ecol. Chem. Eng. S.* 20(1): 69–77.
- Olkowska E., Ruman M., Kowalska A., Polkowska Ż., 2013c, Determination of surfactants in environmental samples Part III. Non-ionic compounds, *Ecol. Chem. Eng. S.* 20(3): 449–461.
- Olkowska E., Polkowska Ż., Ruman M., Namieśnik J., 2015, Similar concentration of surfactants in rural and urban areas, *Environ. Chem. Lett.* 13(1): 97–104.
- Olkowska E., Ruman M., Draj-Śmigalska M., Polkowska Ż., 2017, Selected anionic and cationic surface active agents: case study on the Kłodnica Sediments, *Limnol. Rev.* 17(1): 11–21.
- [SNG] Saur Neptun Gdańsk, 2017, *Wysokość cen i stawek opłat obowiązuująca na terenie miasta Gdańska* (The amount of prices and rates applicable in the city of Gdańsk) [online]. Retrieved from [http://www.sng.com.pl/Portals/2/dok/Formularze/taryfa\\_Gdansk.pdf](http://www.sng.com.pl/Portals/2/dok/Formularze/taryfa_Gdansk.pdf) [accessed 9 October 2017] (in Polish).
- Szmidt K., Bociąg K., 2016, *Wprowadzenie. Zakres i cele projektu „Program kompleksowej ochrony jezior lobeliowych w Polsce. Etap 1. Podstawy, modelowe rozwiązania”* (Introduction. Scope and aims of the project “The programme of comprehensive conservation lobelia lakes in Poland. Step 1. The grounds and showcase solutions”), [in:] Bociąg K., Borowiak D. (eds), *Jeziora lobeliowe w drugiej dekadzie XXI wieku* (Lobelia lakes in the second decade of the 21st century), FRUG, Gdańsk: 7–12 (in Polish, English summary).
- Wilk-Woźniak E., Kraska M., Piotrowicz R., Klimaszuk P., 2012, 3110 Jeziora lobeliowe (3110 Lobelia lakes), [in:] Mróz W. (ed.), *Monitoring siedlisk przyrodniczych. Przewodnik metodyczny. Część druga* (Monitoring of natural habitats. Methodological guide. Part two), GIOŚ, Warszawa: 114–129 (in Polish).
- Ying G.G., 2006, Fate, behaviour and effects of surfactants and their degradation products in the environment, *Environ. Int.* 32(3): 417–431.