*Polish Journal of Environmental Studies Vol. 12, No. 5 (2003), 643-646*

*Letter to Editor*

# Monitoring Surfactant Concentrations in Surface Waters in Tricity Agglomeration

**S. Pastewski, K. Mędrzycka***

Chemical Faculty, Gdańsk University of Technology, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

*Received: 2 January, 2003*
*Accepted: 12 March, 2003*

## Abstract

Studies were conducted to determine the concentration of anionic surfactants in selected waters in Tricity agglomeration (Gdańsk, Gdynia, Sopot). Water samples were taken from November 2001 to May 2002. The total concentration of anionic surfactants in the environmental samples was determined by Methylene Blue Active Substances Method (MBAS). The concentration of anionic surfactants in the analyzed waters ranged from 5 to 150 μg/dm³. The highest surfactant content was observed in the Strzyża stream in Gdańsk and the Kacza river in Gdynia. Less polluted were the Haffner stream in Sopot and the Oliwski stream in Gdańsk.

**Keywords:** anionic surfactants, surface water

## Introduction

The permanent control of the presence of surfactants and their biodegradability in water as well as the permissible concentrations of surfactants in water and wastewater are defined in legal acts [1, 2]. In Poland, permissible concentrations of anionic surfactants in surface waters equal: class I water – 0.2 mg/dm³, class II – 0.5 mg/dm³, class III – 1.0 mg/dm³. Analogue values for non-ionic surfactants equal 0.5, 1.0 and 2.0 mg/dm³, respectively [1]. Concentrations of anionic and non-ionic surfactants in drinking water are also defined (0.2 mg/dm³) [2].

Data concerning the concentrations of surfactants in surface water are rarely published and generally show increasing tendencies in the ratio of non-ionic surfactants vs. anionic surfactants [3, 4]. In Poland, concentration of anionic surfactants was monitored in the Warta river in Poznań between 1990-2000 [5]. Average anionic surfactant concentrations for spring-summer seasons in these years fluctuated around 140 μg/dm³, while for autumn-spring season the average concentration decreased over the last five years from approximately 300 μg/dm³ to approximately 150 μg/dm³ [5]. Similar studies of surfactant concentrations along the Warta river during autumn-winter season of 1997/98 and during the autumn-winter season of 1998/99 were conducted. The determined anionics concentration was in the range 100-304 μg/dm³ [5]. The surfactants content was also investigated in autumn-winter seasons 1997/98 and 1998/99 in the tributaries of the Warta river: Ner, Obra and Noteć. The average surfactant concentrations were as follows: in the Obra river - 70 μg/dm³ (Skwierzyna), in the Noteć river - 75 μg/dm³ (Santok), in the Ner river - 134 μg/dm³ (Stefanów). Much higher anionics concentrations were found in the Ner river, near Dąbie and Poddębice (1700 and 1900 μg/dm³, respectively) close to the urban and industrial area of Łódź [5].

Concentration of anionic surfactants in the rivers of Polish zone of the Baltic Sea (Wisła, Odra, Ina, Reda, Parsęta, Grabowa, Reda, Rega) was analyzed in 1990–1999 by Meteorological and Water Management Institute in Gdynia [6a–6h]. The highest surfactant concentrations were observed in the Wisła river (15–82 μg/dm³) and in the Reda river (8–66 μg/dm³). The less polluted rivers were the Rega river (0–11 μg/dm³), the Grabowa river

*Corresponding author

(12–35 μg/dm$^3$) and the Parsęta river (16–45 μg/dm$^3$). From 1997 a decline of anionic surfactants concentration was observed. In the Wisła river the concentration decreases from 82 μg/dm$^3$ in 1993 to 2 μg/dm$^3$ in 1999, and in the Odra river from 100 μg/dm$^3$ in 1990 to 4 μg/dm$^3$ in 1999. Similar dependencies for other rivers were observed [6a–6h].

The main method recommended in Europe for the determination of total concentration of anionic surfactants in environmental samples is the Methylene Blue Active Substances method (MBAS) [7].

For preconcentration of surfactants and minimization of interferences by nonsurfactant materials, the solvent sublation process is recommended [7, 8]. Solvent sublation is a specific kind of extraction, in which surfactants are transported from water to organic solvent layer by gas bubbles. Their transport is possible thanks to adsorption at the water/gas interface of the bubbles. The bubbles escape into the atmosphere, leaving behind the surfactant dissolved in organic solvent (ethyl acetate). The solvent is separated, dehydrated and evaporated, leaving the surfactant as a residue for analysis.

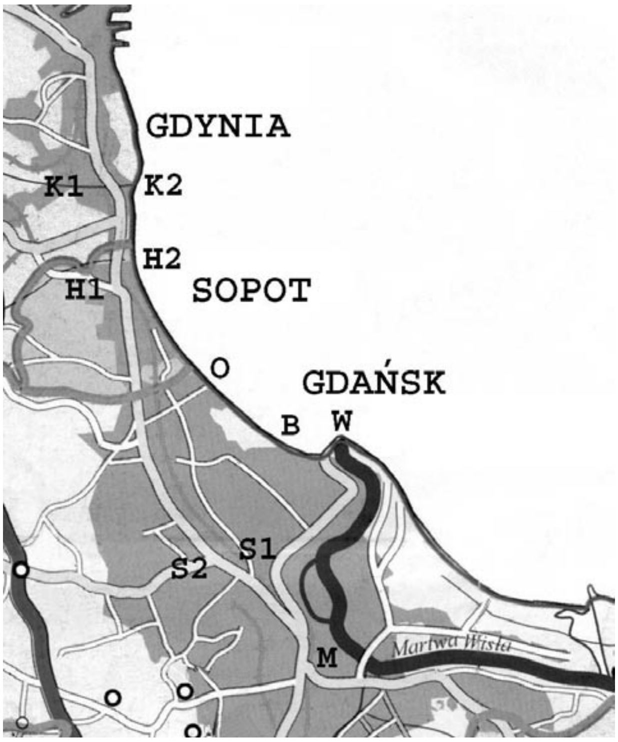


Fig. 1. Sampling sites in Tricity agglomeration.
H1 – the Haffner stream – in the center of Sopot, H2 – the Haffner stream outlet to Gdańsk Bay in Sopot, K1 – the Kacza river – near Powstania Styczniowego Street in Gdynia, K2 – the Kacza river outlet to Gdańsk Bay in Gdynia, M – the Motława river – near Długie Pobrzeże Street in Gdańsk, S1 – Strzyża stream I – near Słowackiego Street in Gdańsk Wrzeszcz, S2 – Strzyża stream II – near Uphagena Street in Gdańsk Wrzeszcz, O – the Oliwski stream outlet in Gdańsk Jelitkowo, W - Gdańsk Bay – coastal waters near the Martwa Wisła in Gdańsk Westerplatte, B - Gdańsk Bay – coastal waters in Gdańsk Brzeźno.

## Experimental

The aim of the investigation was to monitor surfactant concentrations in water in selected rivers in Tricity agglomeration (Gdańsk, Gdynia, Sopot) and along the coast of Gdańsk Bay.

Investigations were conducted from November 2001 to May 2002. Water samples were taken from 10 selected sites in Tricity agglomeration (Fig. 1).

Water was sampled to polyethylene bottles, previously prewashed with methanol and sampling water. The sample volume was about 5 dm$^3$. The water was filtered through a paper filter. First 200 cm$^3$ of filtrate was removed (to prevent an adsorptive loss). Samples were immediately analyzed.

For surfactant separation from interfering compounds and their concentration a solvent sublation technique was used [8]. The apparatus for solvent sublation consisted of 60 mm diameter x 505 mm length glass column, fitted at the bottom with a sintered-glass sparger, used to disperse the gas bubbles. The column was filled with 1 dm$^3$ of water sample. To obtain high surfactant recovery 100 g NaCl and 5 g $NaHCO_3$ were added to the sample. On the top of the aqueous layer 100 cm$^3$ of ethyl acetate was poured. The air flow rate was kept at 1 dm$^3$/min. Sublation was continued for 10 min. Then, the process was repeated with the second 100 cm$^3$ layer of ethyl acetate. Combined ethyl acetate solution was evaporated. The surfactant remained as a film of residue in the flask and was dissolved in methanol and transferred to a 100 cm$^3$ flask, which afterwards was filled with water.

The total concentration of anionic surfactants in the environmental samples was determined by Methylene Blue Active Substances Method (MBAS), according to Polish Standard PN-EN 903 [7]. Extraction into chloroform from acidic aqueous medium containing excess of methylene blue, followed by an aqueous backwash was repeated three times. The absorbance of the separated organic phase was measured spectrophotometrically at a wavelength of maximum absorption of 650 nm.

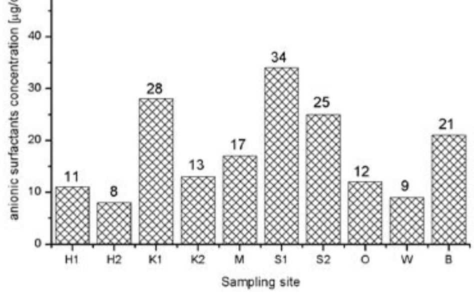


Fig. 2. Anionic surfactants concentration in November 2001.

Recrystalizzed sodium dodecylsulfate (Apollo Scientific Ltd.) was used as standard. Results were recalculated to sodium dodecylbenzenesulfate (LAS) using conversion factor f=0.8276.

## Results

In Figures 2-8, the results of anionic surfactants concentration in water from selected sites from November 2001 to May 2002 are presented. The results are arithmetic mean values from 2 measurements.

In studied water streams in Tricity, the concentration of anionic surfactants was very low, in most cases below 60 μg/dm$^3$. The highest surfactant concentrations (13-150 μg/dm$^3$) were detected in Strzyża stream in the center of Gdańsk Wrzeszcz (in both sampling sites). In a sampling site near Słowackiego street (S1) high fluctuation of anionics concentration in months was observed (13–58 μg/dm$^3$). Higher anionics content (23–150 μg/dm$^3$) was found in the second sampling site – S2 (near Uphagena Street).

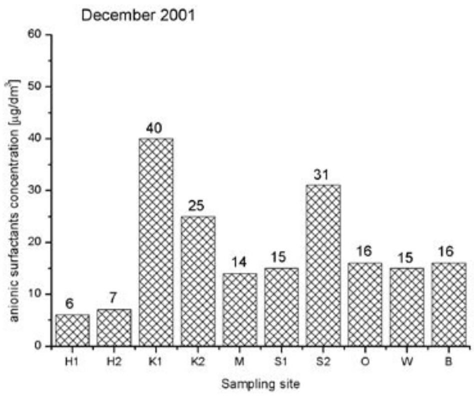


Fig. 3. Anionic surfactant concentrations in December 2001.

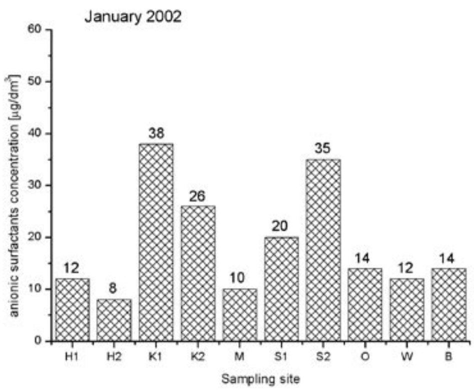


Fig. 4. Anionic surfactant concentrations in January 2002.

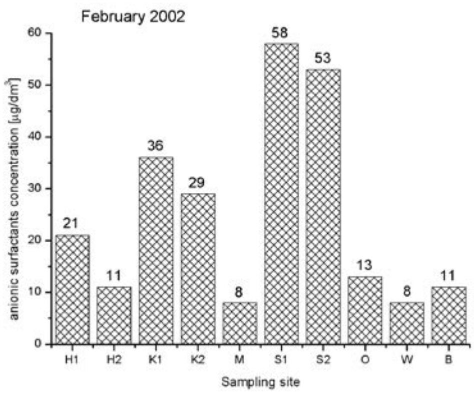


Fig. 5. Anionic surfactant concentrations in February 2002.

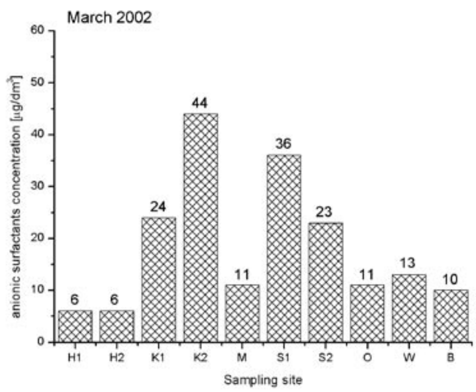


Fig. 6. Anionic surfactant concentrations in March 2002.

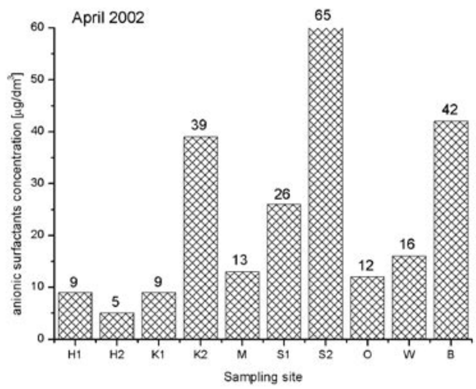


Fig. 7. Anionic surfactant concentrations in April 2002.

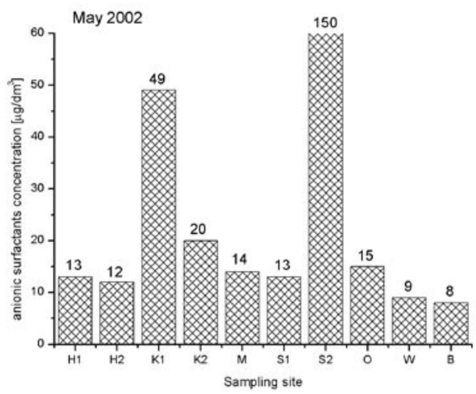


Fig. 8. Anionic surfactant concentrations in May 2002.

The contamination of the Kacza river, localized in Gdynia and Sopot, is similar to that in Strzyża stream. This stream is localized in the center of Tricity, in an area not totally sewered, hence the possibility of pollution by detergents from households and industry is higher than in the case of other rivers. The average concentration of surfactants in the Kacza river was about 30 μg/dm$^3$ and the highest, observed in May 2002, was 49 μg/dm$^3$. Similarly high surfactant contents were observed in the Kacza river outlet to Gdańsk Bay. The highest anionic concentration in this sampling site were observed in March (44 μg/dm$^3$) and in April 2002 (39 μg/dm$^3$).

The low surfactant concentrations (on average 12 μg/dm$^3$) observed in the Motława river in the center of Gdańsk were surprising. The higher values similar to results for the rivers Kacza and Strzyża were expected.

The lowest surfactant contents were observed in Haffner stream in Sopot (on average 10 μg/dm$^3$) and at the outlet of the Oliwski stream in Jelitkowo (on average 13 μg/dm$^3$).

The concentration of anionic surfactants in the coastal water of Gdańsk Bay (in Brzeźno and Jelitkowo) was generally lower (on average 13 and 12 μg/dm$^3$, respectively) than their concentration in the streams (the exceptional high value observed in April in Brzeźno).

The Water Law Act requirements relate also to content of nonionic surfactants. Thus, the concentration of nonionic surfactants in studied streams was also monitored. The total concentration of non-ionic surfactants was determined by Bismuth Active Substance Method (BiAS) according to Polish Standard PN-ISO 7875-2 [9]. However, in all the water streams studied as well as in the coastal waters, the measured concentrations of nonionic surfactants were below detection limit of the BiAS method (200 μg/dm$^3$).

## Conclusions

Concentrations of anionic surfactants between 5 and 150 μg/dm$^3$ were found in the analyzed water streams. The highest content was observed in the Strzyża stream and in the Kacza river. The less polluted water was the Haffner stream in Sopot.

The observed anionics concentration was generally lower in the outlets of the streams and in Gdańsk Bay as a result of higher total volume of water. The dilution factor in the outlet of stream was higher than in the streams and rivers. Dilution factor in rivers is usually higher during the autumn/winter season because the water levels in rivers are higher. This factor can compensate the slower biodegradation rate during these seasons. Finally, analyzed anionic surfactants concentrations do not show seasonal correlations.

The results in all streams do not exceed the permissible values of anionic surfactant concentrations for class I water (200 μg/dm$^3$). Similarly, the concentration of non-ionic surfactants in all investigated samples was much lower than the limit value for class I water, which is 500 μg/dm$^3$.

The pollution of waters by surfactants is low in Tricity agglomeration; the analyzed concentrations are considerably lower than values for the Warta river and their tributaries [5]. Analogically, very low surfactant contents in the rivers of the Polish zone of the Baltic Sea were reported [6].

The very low surfactant contents in analyzed waters probably result from the fact that the industry sector in Poznań area consumes much more surfactants than the industrial sector in Tricity. Besides, in our investigations only small water streams (except the Motława) in the city area were analyzed, while in the case of the Warta river run-off from a greater area affect water quality.

However, it should be underlined that the analytical methods applied are specific for unaltered, original surfactants. Thus, in the case of their alteration due to primary biodegradation, these surfactants give no response to analytical reagent (e.g. methylene blue), while the products of incomplete biodegradation may still be present in water [10, 11]. On the other hand, it was proved that even if biodegradation is not complete the toxic effect to aquatic organisms is almost totally reduced after primary biodegradation. Biodegradation decreases surfactant content in surface water and its rate depends on water temperature and living conditions for micro-organisms responsible for biodegradation. However, significant changes of surfactant concentrations in relation to temperature changes in particular seasons were not observed during the experimental period.

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