

Surfactants in the River Warta: 1990-2000

A. Szymanski, B. Wyrwas, A. Jesiolowska, S. Kazmierczak, T. Przybysz,
J. Grodecka, Z. Lukaszewski

Poznan University of Technology, Institute of Chemistry,
ul. Piotrowo 3, Pl-60-965 Poznan, Poland

Received: 5 April, 2001

Accepted: 4 May, 2001

Abstract

Data concerning the systematic determination of anionic surfactants (AS) and non-ionic surfactants (NS) over the period 1990-2000 in a single sampling point (Poznan) is reported, as well as data concerning the determination of these surfactants along the whole of the River Warta measured in 1997-1999. The indirect tensammetric method was applied for the determination of non-ionic surfactants, while the MBAS method was applied for the determination of anionic surfactants. The average concentration of NS over the period 1990-2000 showed a highly increasing tendency, from approximately $25 \mu\text{g l}^{-1}$ to approximately $150 \mu\text{g l}^{-1}$. The average spring-summer concentration of AS over this period fluctuated around the value of $140 \mu\text{g l}^{-1}$, while autumn-winter average concentrations showed a gradual decrease in average concentration over the last five years, from approximately $300 \mu\text{g l}^{-1}$ to approximately $150 \mu\text{g l}^{-1}$.

Keywords: anionic surfactants; non-ionic surfactants; surface water.

Introduction

Data concerning the concentration of surfactants in surface water are rarely published, despite the fact that they constitute a massive stream of anthropogenic organic carbon directed to the water environment. Most available data were published in the 1980s [1] and showed a general increase in the ratio of non-ionic surfactants(NS) vs. anionic surfactants (AS). Both types of surfactants demonstrated a relatively low level of concentration. Current tendencies in washing powder formulation show an increase in NS consumption due to better detergency at lower temperature and lower vulnerability to water hardness [2]. If generally poorer NS biodegradation is taken into account, the substantial change in NS/AS ratio, as well as an increase in total surfactant concentration should be expected. No data concerning systematic screening of surfactants in Polish rivers have been published to date.

The River Warta is the main tributary of the River Odra and collects surface water from a large part of the

country, including effluents from the Poznan area and to a lesser extent from the Lodz area, as well as Silesia (Fig. 1). Very few data concerning surfactants in the River Warta have been published [3, 4].

In this work, data concerning the systematic determination of AS and NS over the period 1990-2000 in a single sampling point (Poznan) is reported, as well as data concerning the determination of these surfactants along the whole of the River Warta measured in 1997-1999.

The possibility of screening AS and NS in river water is closely related to the development and cost of analytical methods. The simple and inexpensive Methylene Blue Active Substances method (MBAS) is used for AS determination [5]. However, the MBAS has been replaced to some degree by a specific linear alkylbenzene sulphonate (LAS) determination by gas-chromatography (GC) or liquid chromatography (HPLC) [6]. LAS is the major AS in terms of output [2, 7]. The ratio of LAS/AS differs in different parts of the river [1]. Determination of LAS alone provides fragmentary information. Specific methods for the determination of other major AS, such as alkyl sulphates or alkylether sulphates have not as yet been introduced into the analytical routine.

Methods for NS determination are usually more complex than those for AS determination. The Bismuth Active Substances method (BiAS) [8] or Cobalt Thiocyanate Active Substances method (CTAS) [5] are recommended for NS determination in Europe and the USA, respectively. Both methods are better suited for NS in sewage determination than in surface water [9]. The BiAS, applied to NS determination in river water requires the processing of a 4 litre sample and the evaporation of approximately half a litre of ethyl acetate.

The HPLC methods are applied for the specific determination of alkylphenol ethoxylates and alcohol ethoxylates. Alcohol ethoxylates (AE), being the major NS, need to be derivatised prior to determination because they lack a chromophoric group [10]. The hyphenated HPLC-mass spectrometry (HPLC-MS) technique can be applied for AE determination without derivatisation [11]. However, the results of the HPLC methods are considerably lower than the BiAS or CTAS methods.

Tensammetric methods are considerably less costly in comparison to BiAS or CTAS and especially HPLC or HPLC-MS. The ratio of the apparatus cost of tensammetric methods in comparison with HPLC or HPLC-MS is as 1:10:50. Tensammetric methods are tailored to the determination of NS and produces results similar to those of the BiAS or CTAS. The indirect tensammetric method (ITM) is the simplest method for NS determination in river water [3]. A more specific method combining the BiAS separation scheme with the indirect tensammetric measurement (BiAS-ITT) is more time and labour consuming [12]. Therefore, in this work the ITM was applied for the majority of measurements and the BiAS-ITT was applied as a reference method.

Experimental

Apparatus

Electroanalytical Instruments

A Radelkis OH-105 polarograph and an ECO Chemie General Purpose Electroanalytical System μ AUTOLAB were alternatively used for tensammetric measurements. Controlled-temperature HMDE equipment (Radiometer), having an additional platinum wire auxiliary electrode, was used. A quartz beaker instead of a glass one and protection of ceramic frit on the end of a salt bridge were applied to prevent an adsorptive loss of surfactant [13]. *Spectrophotometer*

A Carl-Zeiss Jena Specord M40 UV-Vis spectrophotometer was used.

Materials and Methods

Seventeen sampling points (SP) shown in Fig. 1A were selected along the River Warta (SP 1-17), three additional SP along the River Ner (SP 7a, 7b and 7c), SP at the Rivers Obra and Notec (SP 13a and 14a, respectively) at the river confluences to the River Warta, as well as SP at the River Odra upstream to the confluence with

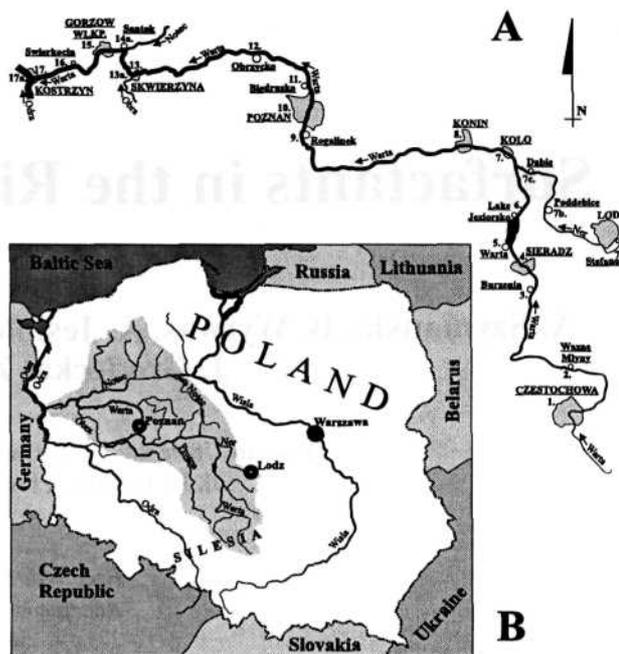


Fig. 1. (A) Sampling points along the River Warta and its tributaries; (B) The River Warta Basin.

the River Warta (SP 17a). At the SP Poznan, located at the Roch Bridge, samples were taken regularly over the period of 1990-2000, with approximately one month intervals. Research concerning the River Warta upstream from Poznan (including SP Biedrusko, located downstream Poznan) was performed during the autumn-winter season of 1997/98 while the other part of the work was performed during the autumn-winter season of 1998/99. Samples were taken three times for each SP with an interval of approximately six weeks.

The river water was sampled from 1 m depth. Samples were immediately preserved with 1% formaline.

Standards

Triton X-100 (deca(ethylene glycol)mono[4-(1,1,3,3-tetra methylbutyl)phenyl] ether) (Rohm and Haas) and sodium dodecylbenzene sulphonate (Fluka) were used as standards without additional purification. *Other reagents and materials*

Purified sodium sulphate and sodium chloride were used for the preparation of the aqueous base electrolytes. All solutions used in analysis were prepared in water triply distilled from a quartz apparatus. Only freshly distilled water was used.

Freshly distilled ethyl acetate and chloroform were used. Other reagents used were of Analar grade, as were methanol and sodium hydrogencarbonate.

The other reagents used were of Analar grade.

Procedures

Separation of non-ionic surfactants from the water samples
400 ml of water were taken for each analysis. The water was filtered through a paper filter. The first half of the filtrate was removed (to prevent an adsorptive loss) while 200 ml from the other half were taken for further

processing. 20 g of sodium chloride and 1 g of sodium hydrogencarbonate were dissolved in the sample and the solution was transferred into a separation funnel. 20 ml of ethyl acetate were added and the extraction of NS was performed. The extraction was repeated with the next 20 ml portion of the solvent. Both portions of ethyl acetate were collected in a volumetric flask for 50 ml and the flask was made up to the mark with ethyl acetate. Aliquots of the extract were used for the ITM measurements.

Determination of total concentration of NS by the indirect tensammetric method

The aliquot of the extract, usually equivalent to approximately 10 μg of NS was evaporated in a small beaker. The residue was dissolved in 1.5 ml of ethyl acetate and transferred to a 25 ml volumetric flask, 12.5 ml of 1 M aqueous sodium sulphate was added and the flask was made up to the mark with water. The mixture containing excess of ethyl acetate was vigorously shaken and the emulsion transferred into the voltammetric cell. The emulsion was stirred for 10 min to achieve clarity of the solution due to evaporation of the excessive ethyl acetate. This excessive ethyl acetate extracts surfactants, therefore it must be removed and this is evidenced by the disappearance of turbidity. After a quiescent period (30 sec) the tensammetric curve of ethyl acetate was recorded in the cathodic direction starting from -1.20 V (vs. SCE) using a new mercury drop. The difference between the height of the peak of ethyl acetate (recorded in a separate measurement) and the peak height of ethyl acetate in the presence of NS is the analytical signal. The results were quantified using a calibration curve of Triton X-100.

Reference method for the determination of total concentration of NS

The indirect tensammetric technique combined with the BiAS separation scheme was used as a reference method [4].

Determination of total concentration of AS

This was performed according to the MBAS standard procedure [5] using sodium dodecylbenzene sulphonate as the standard.

Results

The measurements of AS and NS concentration in the River Warta in Poznan were performed over the period 1990-2000 with an average frequency of one measurement per month. The results of a one year period are given in Table 1 as an example. The average values for both AS and NS over the autumn-winter (October-March) season are significantly higher than those for the spring-summer (April-September) season. This is a rule for all the results. Therefore, the results for autumn-winter seasons have been processed separately from the results for spring-summer seasons. In order to show the results more clearly, the average values of autumn-winter and spring-summer seasons were calculated (usually on the basis of 6 results) and put in the graphs of results. The results concerning AS are shown in Figs. 2a and 2b and those concerning NS are shown in Figs. 3a and 3b,

for spring-summer seasons and autumn-winter seasons, respectively.

The average AS concentration for spring-summer seasons (Fig. 2a) shows no clear tendency over the ten year period and fluctuates around the value of 140 $\mu\text{g l}^{-1}$. The average AS concentration for autumn-winter seasons (Fig. 2b) shows a different pattern: the gradual decrease in average concentration over the last five years from approximately 300 $\mu\text{g l}^{-1}$ to approximately 150 $\mu\text{g l}^{-1}$.

The pattern for NS average concentration is completely different than for AS. Average concentration for both spring-summer seasons and autumn-winter seasons (Figs. 3a and 3b) shows a highly increasing tendency from approximately 25 $\mu\text{g l}^{-1}$ to approximately 150 $\mu\text{g l}^{-1}$.

The measurements of AS and NS concentration were performed at 17 sampling points along the River Warta. Measurements were performed during the autumn-winter season of 1997/98 (samples points upstream of Poznan) and during the autumn-winter season of 1998/99 (samples points downstream of Poznan). The reason for this division was lack of financial support sufficient to perform all experiments at one time. An average value for each sampling point was determined on the basis of three analyses done with an interval of approximately six weeks. The results are shown in Fig. 4. The results for the River Warta have been supplemented with the results for the River Ner, the River Notec and the River Obra, all three being major tributaries of the River Warta, as well as the result for the River Odra. The River Ner was screened along the whole length in order to observe the impact of the Lodz urban and industrial area. The Rivers Notec, and Obra were screened at their confluences with the River Warta while the River Odra was screened several kilometres upstream to its confluence with the River Warta. The results are shown in Figs. 5a and 5b.

Table 1. Concentration of anionic surfactants (AS) and non-ionic surfactants (NS) in the River Warta: 31 October 1996 - 30 September 1997.

Date	AS [$\mu\text{g l}^{-1}$]	NS [$\mu\text{g l}^{-1}$]
31.10.1996	130	90
29.11.1996	110	100
31.12.1996	700	95
31.01.1997	450	105
03.03.1997	160	120
16.03.1997	320	105
Average	310	105
01.04.1997	120	110
29.04.1997	110	95
30.05.1997	120	85
01.07.1997	140	75
01.08.1997	100	50
29.08.1997	90	125
30.09.1997	110	70
Average	110	85

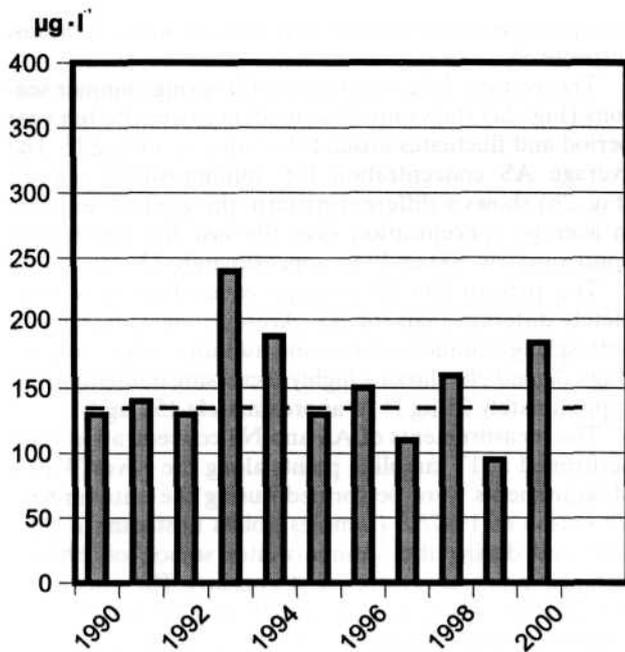


Fig. 2a. Anionic surfactants in the River Warta, Poznan (average values for spring-summer periods).

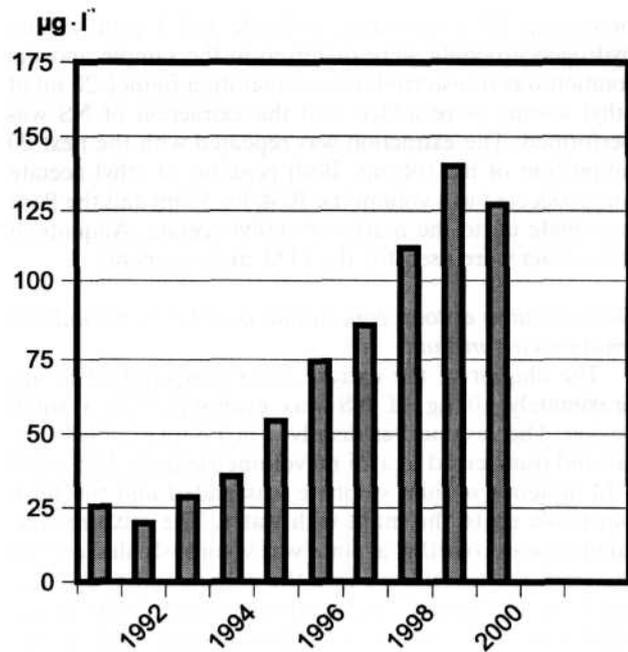


Fig. 3a. Non-ionic surfactants in the River Warta, Poznan (average values for spring-summer periods).

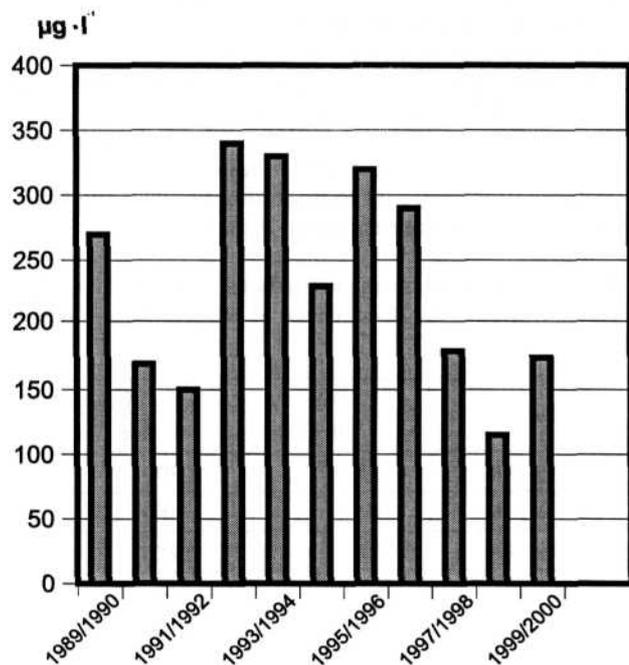


Fig. 2b. Anionic surfactants in the River Warta, Poznan (average values for autumn-winter periods).

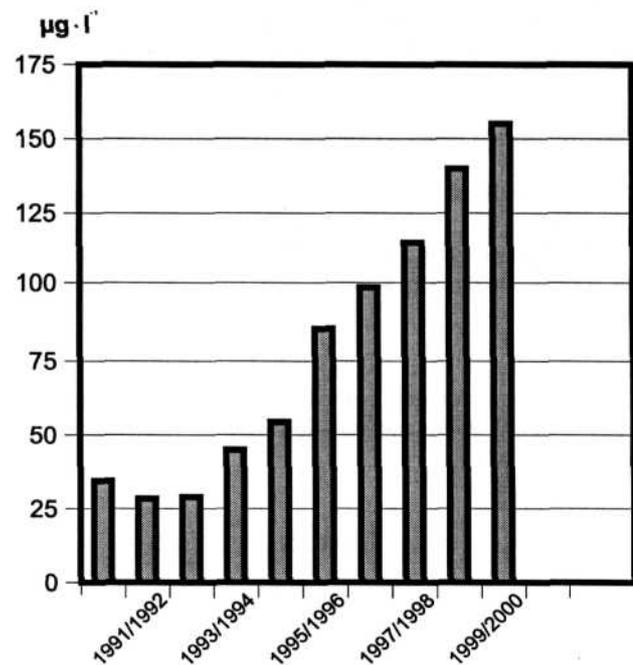


Fig. 3b. Non-ionic surfactants in the River Warta, Poznan (average values for autumn-winter periods).

Apart from several sampling points, concentration of AS and NS showed a relatively stable level along the whole River Warta. 11 of 16 results for AS and 8 of 16 results for NS were within the range of 100-150 $\mu\text{g l}^{-1}$. Thus, AS and NS concentrations were at the same level of concentration. Distinctly higher NS concentrations

were recorded downstream of the industrial towns of Czestochowa, Sieradz and Gorzow. The impact of the Poznan urban and industrial area (pop. 650 000) on NS concentration was unexpectedly small but it was more pronounced for AS concentration. The impact of the Lodz urban and industrial area (pop. 850 000) was dis-

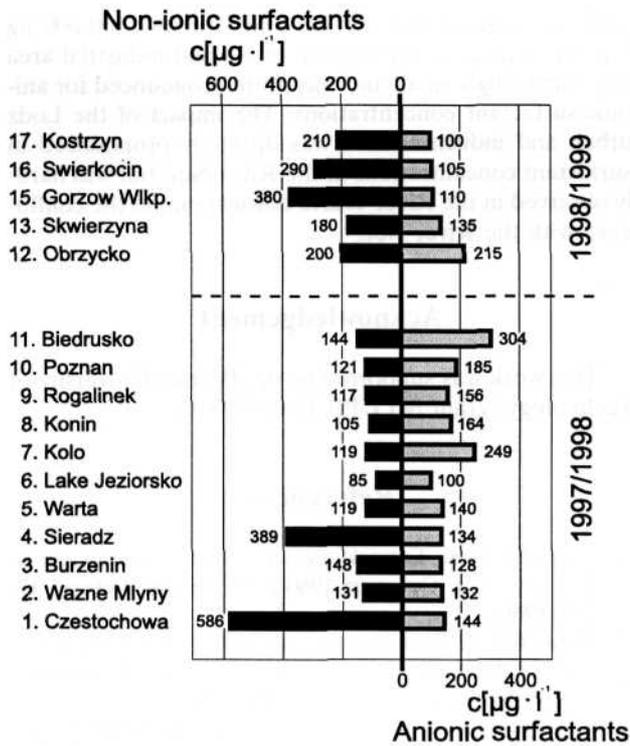


Fig. 4. Anionic surfactants and non-ionic surfactants along the River Warta (autumn-winter periods 1997-1999).

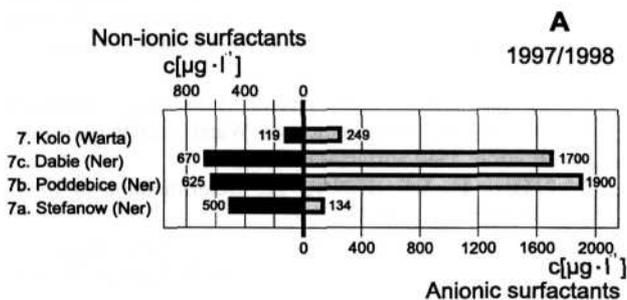
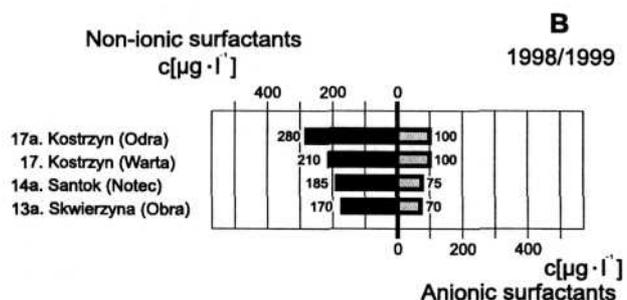


Fig. 5a. Anionic surfactants and non-ionic surfactants along the River Ner (the autumn-winter period 1997/98). The data for the River Warta is given for comparison.

Fig. 5b. Anionic surfactants and non-ionic surfactants in the



River Odra, the River Notec and the River Obra (the autumn-winter period 1998/99). The data for the River Warta is given for comparison.

tinctly pronounced in AS and NS concentration in the River Ner. In terms of AS concentration, the values were more similar to those of a raw sewage than surface water. Surprisingly, this high flux of surfactants was hardly observed in the River Warta downstream to the confluence with the River Ner (sampling point at Koto). Only AS concentration was slightly above average level. Even this impact was not observed at the further sampling point downstream the river (at Konin). This is evidence of the high biodegradative ability of the River Warta in respect to surfactants. Concentrations of AS and NS in the Rivers Notec and Obra were very similar to those in the River Warta in the vicinity of the confluences. The River Odra, several kilometres upstream to its confluence with the River Warta showed higher NS concentration and similar AS concentration to the River Warta in its lower part.

Discussion

Surfactant concentration in river water is determined by three major factors:

- i) a flux of surfactant to surface water,
- ii) total volume of surface water,
- iii) biodegradation rate.

An adsorption on particles suspended in river water, on a water-air interface and on the river bed also plays a certain role, but less significantly than the above mentioned factors. The biodegradation rate depends on water temperature and living conditions for micro-organisms responsible for biodegradation. The ten year screening of AS and NS at the sampling point at Poznan, shown in Figs. 2 and 3, reflects the total effect of all these factors. The tendencies observed in these Figs, reflect long-term changes in consumption levels and in qualitative changes in surfactant manufacture. Generally, stable AS levels over spring-summer seasons and decreasing tendency over autumn-winter seasons is observed as well as strongly increasing tendency for NS. This is in agreement with general trends in the manufacture of surfactants [2] and slower biodegradation of NS than AS [14]. Due to these trends, the AN/NS ratio in the river water gradually shifted to the advantage of NS. Currently, concentrations of both types of surfactants represent a similar level of concentration. Future projection shows that NS may soon be the dominant surfactant in surface water.

As for the dilution and biodegradation factors, the latter was dominating over the dilution factor. Despite a higher dilution factor during the autumn-winter seasons (the river level was usually much higher during those seasons), lower average surfactant concentration during spring-summer seasons was observed, which indicates that the biodegradation factor dominated over the dilution factor.

Adsorption on particles suspended in river water for the River Warta was investigated during 1994-1995 and published elsewhere [4]. The flux of NS adsorbed on particles was on average 20% of the total NS flux in the River Warta.

The question arises whether the pattern shown in Figs. 2 and 3 was typical or specific for local conditions of

the sampling point Poznan (Poznan City). The data in Figs. 4 and 5 show that AS and NS concentrations measured at the sampling point Poznan are rather typical of the whole River Warta. Moreover, the major tributaries (the River Notec and the River Obra) represent a very similar level of concentration of both surfactant types. Hence, the trends observed at the Poznan sampling point were characteristic of Western Poland over the period 1990-2000.

Considering the AS/NS ratio it is necessary to stress the relative character of this value. A total concentration of both NS and especially AS depends on the composition of a mixture (which is unknown) and on the choice of standard surfactant. The latter problem was discussed elsewhere in detail [15]. NS concentration measurement by the indirect tensammetric method is only slightly vulnerable to the choice of standard. On the other hand, AS determination by the MBAS method is highly vulnerable to this factor. If sodium lauryl sulphate is used as the standard in the determination instead of sodium dodecylbenzene sulphonate, the results are approximately twice lower. Additionally, the MBAS result of AS concentration indicates a positive error due to the presence in river water of natural substances (called pseudosurfactants) giving the analytical response such as AS.

An appearance of poly(ethylene glycols) (PEG) in river water is a side effect of growing NS concentration. PEG are a by-product of NS biodegradation. Concentrations of the order of 150-250 $\mu\text{g l}^{-1}$ in the River Warta and the River Odra were reported [16]. A further increase in PEG concentration is expected as a consequence of growing NS concentration.

The indirect tensammetric method used over ten years for the determination of NS concentration has proved itself as a reliable, inexpensive analytical method. Only 400 ml of sample is required and reagent consumption is ten-times lower than in the case of the classical BiAS method. The determination can be completed in 1 hour and even this time may be substantially reduced in serial analysis.

Conclusions

1. Average concentrations of non-ionic surfactants over the period 1990-2000 showed a highly increasing tendency from approximately 25 $\mu\text{g l}^{-1}$ to approximately 150 $\mu\text{g l}^{-1}$.

2. The average spring-summer concentration of anionic surfactants over the period 1990-2000 fluctuated around the value of 140 $\mu\text{g l}^{-1}$, while autumn-winter average concentrations showed a gradual decrease in average concentration over the last five years from approximately 300 $\mu\text{g l}^{-1}$ to approximately 150 $\mu\text{g l}^{-1}$.

3. For the majority of sampling points, concentration of anionic surfactants and non-ionic surfactants showed a relatively stable level along the whole of the River Warta (100-150 $\mu\text{g l}^{-1}$) and concentrations of both types of surfactant were at the same level of concentration.

4. Distinctly higher concentrations of non-ionic surfactants were recorded downstream of industrial towns

such as Czestochowa, Sieradz and Gorzow (400-600 $\mu\text{g l}^{-1}$). The impact of the Poznan urban and industrial area was surprisingly small and was more pronounced for anionic surfactant concentrations. The impact of the Lodz urban and industrial area was distinctly pronounced in surfactant concentrations in the River Ner, but was hardly observed in the River Warta downstream to the confluence with the River Ner.

Acknowledgement

This work was supported by the Poznan University of Technology (grant No DPB 31-605/2001).

References

1. FISCHER W.K., Entwicklung der Tensidkonzentrationen in den deutschen Gewässern 1960-1980, *Tenside Deterg.*, **17**, 250, **1980**
2. PALICKA J., Development and Trends in the European Laundry Detergent Market, III International Symposium: Chemistry Forum'97, Warsaw, April, **1997**
3. SZYMANSKI A., WYRWAS B., LUKASZEWSKI Z., Application of an Indirect Tensammetric Method for the Determination of Non-Ionic Surfactants in Surface Water. *Anal.Chim.Acta*, **305**, 256, **1995**
4. WYRWAS B., SZYMANSKI A., LUKASZEWSKI Z., Determination of Non-Ionic Surfactants Adsorbed on Particles of Surface Water by an Indirect Tensammetric Method Combined With BiAS Separation Scheme, *Anal.Chim.Acta*, **331**, 131, **1996**.
5. APHA, American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 18th Edition, 5540 Surfactants, **1992**.
6. MATTHIJS E., DE HENAU H., Determination of LAS, *Tenside Surf. Det.*, **24**, 193, **1987**.
7. SCHULZE K., *Tenside Surf. Det.*, Der Westeuropasche Tensidmarkt 1994/95, (West European Surfactant Market 1994/95), **33**, 94, **1996**.
8. WICKBOLD R., Zur Bestimmung nichtionischer Tenside in Fluss- und Abwasser (On the Determination of Non-Ionic Surfactants in River Water and Sewage). *Tenside Deterg.*, **9**, 173, **1972**.
9. BROWN D., DE HENAU H., GARRIGAN J.T., GERIKE P., HOLT M., KECK E., KUNKEL E., MATTHIJS E., WATKINSON R.J. Removal of Nonionics in a Sewage Treatment Plant. *Tenside Deterg.*, **23**, 190, **1986**.
10. ZANETTE M., MARCOMINI A., MARCHIORI E., SAMPERI R., High-Performance Liquid Chromatographic-Fluorescence Determination of Aliphatic Alcohol Polyethoxylates and Poly(ethylene Glycols) in Aqueous Samples, *J.Chromatogr.A*. **756**, 159, **1996**.
11. CRESCENZI C., DI CORCIA A., MARCHIORI E., SAMPERI R., MARCOMINI A., Determination of Nonionic Polyethoxylate Surfactants in Environmental Waters by Liquid Chromatography/Electrospray Mass Spectrometry, *Anal.Chem.*, **34**, 1797, **1995**.
12. WYRWAS B., SZYMANSKI A., LUKASZEWSKI Z., Tensammetric Determination of Non-Ionic Surfactants Combined With BiAS Separation Procedure (Wickbold) - II. Optimisation of the Precipitation and Investigation of Interferences. *Talanta*, **42**, 1251, **1995**.

13. SZYMANSKI A, LUKASZEWSKI Z., Tensammetry with Accumulation on the Hanging Mercury Drop Electrode. Part 6. Errors of Determination Caused by Adsorption of Non-Ionic Surfactants on the Material of the Measuring Cell, *Anal.Chim.Acta.*, **231**, 77, **1990**.
14. SIWINSKI P., SZYMANSKI A., LUKASZEWSKI Z., Biodegradability of Detergent Powder Surfactants in the River Water Die-Away Test, *Polish J.Environ.Studies*, **7**, 251, **1998**.
15. LUKASZEWSKI Z., SZYMANSKI A., Sources of Error in the Determination of Non-Ionic Surfactants in Environmental Samples, *Mikrochim.Acta*, **123**, 185, **1996**.
16. SZYMANSKI A, WYRWAS B., SZYMANOWSKA M., LUKASZEWSKI Z., Determination of short-chained poly(ethylene glycols) and ethylene glycol in environmental samples, *Water Res.*, 35, 3599, **2001**.