

Annual Changes of Basic Parameters of Bottom Sediments from the Klodnica River Catchment

Ewa Olkowska ¹⁺, Marek Ruman ² and Żaneta Polkowska ¹

¹ Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12 Str., 80-233 Gdańsk, Poland

² Earth Sciences Faculty, University of Silesia, Będzińska 60 Str., 41-200 Sosnowiec, Poland

Abstract. The Klodnica River Catchment is heavily contaminated ecosystem located in area of the Upper Silesia Industrial Region. In this area various forms of human activity can be observed (e.g. mining coal underground, metallurgy, power/heat plants, wastewater discharged directly into the river). The impact of industrial and municipal wastes on this aquatic system causes to changes in the hydrographic network of river and the waters quality.

In present study, the annual changes of basic physicochemical parameters (pH, electrical conductivity, inorganic ions, different type of organic compounds e.g. cationic surfactants) of bottom sediments collected in area of the Klodnica River Catchment were investigated. These research aims can provide the knowledge to expand areas of research in order to protect abiotic and biotic elements of the environment and the possibility of using them in a sustainable manner.

Keywords: Bottom sediment, the Klodnica River, physicochemical parameters, cationic surfactants.

1. Introduction

The development of civilization related to increasing industrialization and migration to urban areas, causes negative impacts on quality of different environmental compartments [1]. As a consequence of development of civilization, more and more expanded range of chemical substances is applied in different areas of human activities which inevitably leads to emissions of various pollutants (basic chemical or its degradation products) to individual elements of the environment, in particular to surface waters.

A wide range of anthropogenic pollutants has been detected in the aquatic systems [2]. Bottom sediments are element of the environment, where pollutants emitted from anthropogenic activity can be accumulated and undergo various physicochemical processes. Those processes may potentially cause degradation of quality of abiotic ecosystems and negative effects in aquatic organisms [1], [3]. Additionally, the positively charged contaminants (e.g. pesticides, pharmaceuticals and cationic surface active agents) may undergo of sorption processes to environmental surfaces like soils or bottom sediments, which possess a negative surface charge [4]-[6].

The Klodnica River Catchment is heavily contaminated aquatic system located in area of the Upper Silesia Industrial Region. River is located in area with the occurrence of various forms of human activity (e.g. mining coal underground, metallurgy, power plants, wastewater discharged directly into the river). The impact of industrial and municipal wastes on this ecosystem is observed as changes in the hydrographic network of river and the quality of its waters. In addition, pollutants are introduced into the river along with the runoff waters from heavily urbanized areas [7], [8].

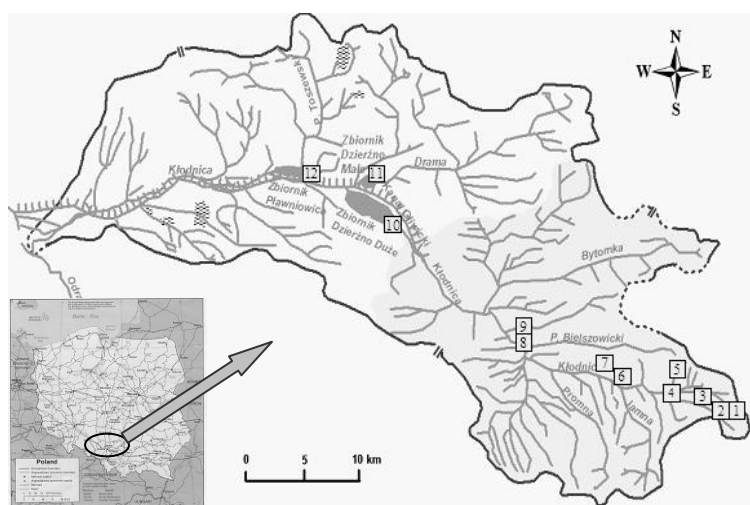
⁺ Corresponding author. Tel.: + 48 58 347 21 10; fax: +48 58 347 26-94.
E-mail address: ewaolkow@wp.pl.

In present research, the annual changes of basic physicochemical parameters (pH, electrical conductivity, inorganic ions, different type of organic compounds e.g. cationic surfactants) of bottom sediments collected in area of the Klodnica River Catchment were investigated. These research aims can provide the knowledge base to expand areas of research in order to protect aquatic ecosystems and the possibility of using them in a sustainable manner.

2. Materials and Methods

All chemicals used during experimental stages were supplied by Merck (Frankfurt/Main, Germany) or Sigma-Aldrich (St. Louis, USA). Deionized water (18 MΩ/cm) was obtained from a Milli-Q system (Billerica, USA).

Annual changes of sediment quality (based of determination of different parameters) were investigated in area of the Klodnica River Catchment (Southern Poland). The area covered by presented study is shown in Fig. 1. The bottom sediments samples were collected during the years 2012 (9 sampling points) and 2013 (12 sampling points).



No. Localization of sampling points

1	50°12'1.60"N 19°02'1.21"E
2	50°12'71,6"N 18°59'62,2"E
3	50°12'71,5"N 18°59'61,1"E
4	50°13'43,00"N 18°55'82,4"E
5	50°13'96,2"N 18°57'22,3"E
6	50°14'01,9"N 18°52'17,6"E
7	50°14'12,3"N 18°51'52,5"E
8	50°15'18,3"N 18°45'30,3"E
9	50°15'26,8"N 18°45'22,0"E
10	50°21'44,92"N 18°33'42,13"E
11	50°23'19,46"N 18°33'53,00"E
12	50°23'34,07"N 18°29'33,96"E

Fig. 1: Sampling point located in area of the Klodnica River Catchment

After samples collection stage they were transported to laboratory and lyophilized. The solid samples were kept frozen at -20 °C until analysis. Next, water extracts were prepared and analyzed with use of the analytical protocol presented in Fig. 2.

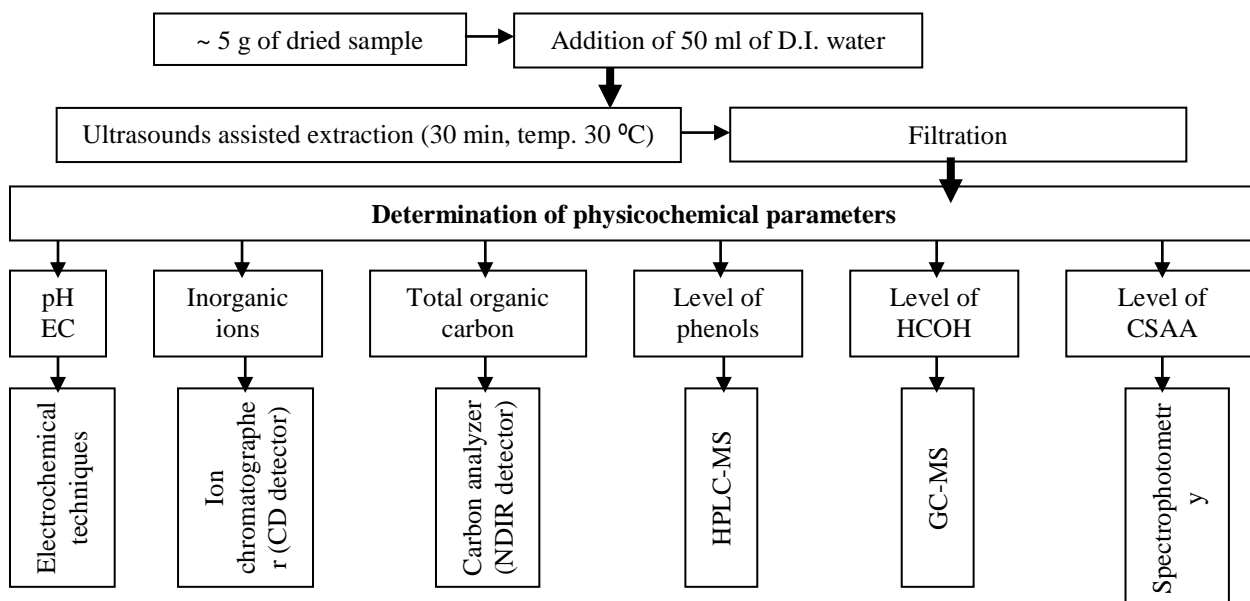


Fig. 2: The analytical protocol for determination selected parameters in sediment samples [5], [7]

3. Result and Discussion

Basic statistic analysis of obtained results for samples from the Klodnica River Catchment was conducted. The selected inorganic and organic physicochemical parameters of sediment samples are presented in Table 1 and 2, respectively.

Table 1: The selected inorganic physicochemical parameters of sediment samples [mg/g sample]

	pH	EC ^a	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	Mg ²⁺	K ⁺	Ca ²⁺
Sediments 2012													
Min	6.31	118	0.034	0.027	0.010	0.010	0.0038	0.10	0.014	0.006	0.0046	0.0056	0.046
Max	7.31	1633	0.054	2.3	0.017	0.024	0.14	3.9	1.06	0.20	0.26	0.19	0.72
Mean	6.64	439	0.042	0.51	0.012	0.017	0.024	1.0	0.22	0.056	0.047	0.064	0.196
SD	0.371	486	0.0069	0.91	0.0066	0.010	0.042	1.2	0.30	0.061	0.079	0.069	0.21
Sediments 2013													
Min	5.81	210	0.034	0.028	0.0098	0.0097	0.0031	0.064	0.0099	0.0054	0.00074	<LOD	0.0143
Max	8.34	1920	0.085	0.16	0.010	0.014	0.015	14	0.11	0.035	0.036	0.059	0.1269
Mean	6.88	820	0.042	0.060	0.010	0.011	0.0060	2.4	0.040	0.010	0.010	0.012	0.0420
SD	0.531	450	0.015	0.036	0.0051	0.0053	0.0035	5.0	0.033	0.0082	0.0085	0.020	0.0289

^a [μS]

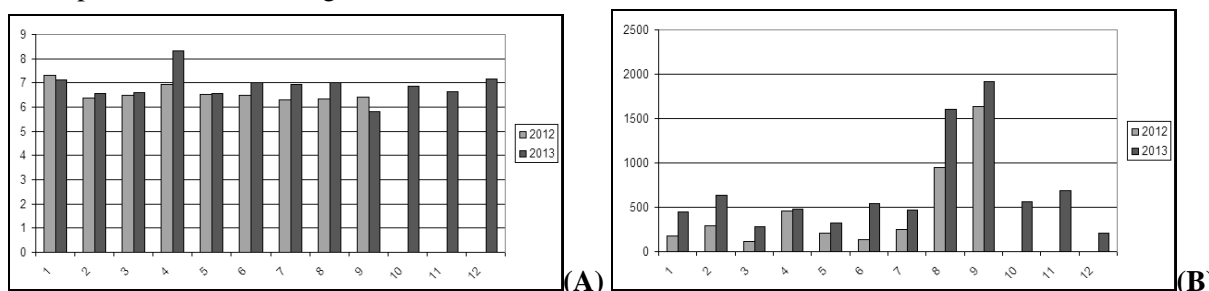
Table 2: The selected organic physicochemical parameters of sediment samples [mg/g sample]

	pH	EC	TOC	Phenols	HCOH	Cationic surfactants
Sediments 2012						
Min	6.31	118	5.7	0.0020	0.0016	0.0003
Max	7.31	1633	154	0.0052	0.012	0.0169
Mean	6.64	439	72	0.0030	0.0050	0.0057
SD	0.371	486	48	0.0014	0.0029	0.0003
Sediments 2013						
Min	5.81	210	0.072	0.00205	0.0016	0.00030
Max	8.34	1920	63	0.00525	0.0119	0.0079
Mean	6.88	820	25	0.00300	0.0050	0.0017
SD	0.531	450	19	0.00140	0.0029	0.0003

^a [μS]; ^b [mg C/L]

The annual changes of selected parameters in sediment samples is presented on Fig. 3. In all water extracts were detected analytes, which were covered by research. The range of pH values in samples collected in 2013 were wider than in 2012. Electric conductivity is higher for samples from 2013. The concentration of inorganic ions depending on their type was different in series of samples collected in mentioned two years. In sampling points number 8 and 9 collected sediments contain highest values of inorganic ions. Also electric conductivity for samples collected in mentioned points is higher than in other sides.

Sum of organic compounds is lower for samples collected in 2013 year. The concentration of organic analytes is higher in samples (with number 16-18) collected in 2013. Those liquid samples were taken from reservoir or lake. It can be noted that such systems with reduced water exchange level of pollutant concentrations are higher than in other river parts. The concentration level of cationic surface active agents in sediments samples is lower in 2013. Samples collected in sampling point number 3 and 8 contain the higher amount of those pollutants. Further stage in determination pollution degree in research area should be determination of individual concentration of cationic surfactants. This aspect will be conducted with use of previous presented methodologies [5], [9].



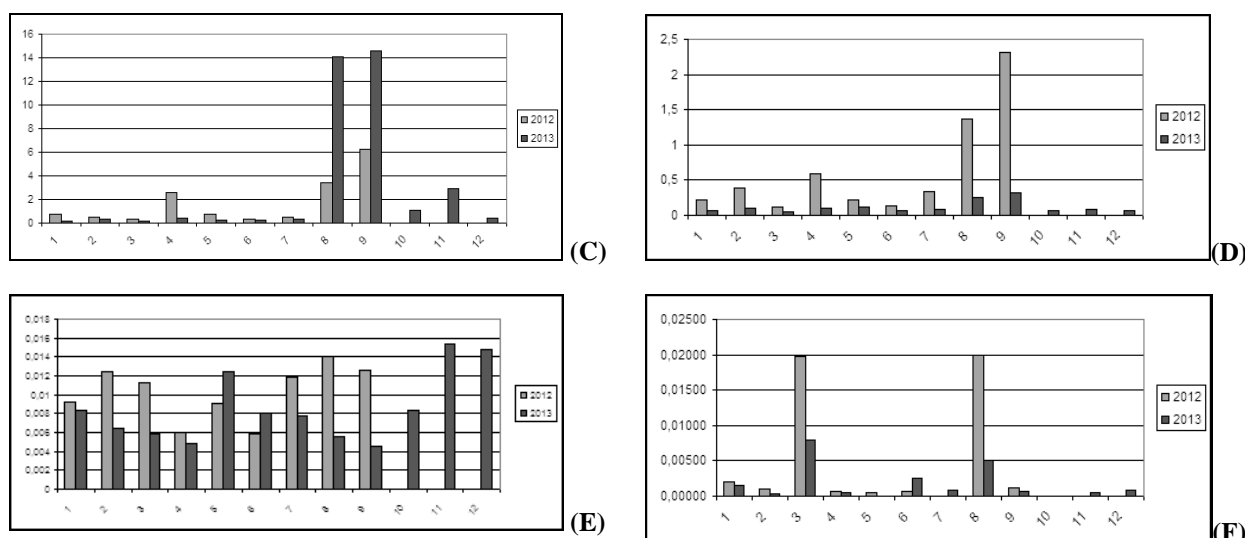


Fig. 3: The annual changes of selected parameters in sediment samples: (A) – values for pH; (B) – values for EC; (C) – sum of inorganic anions; (D) – sum of inorganic cations; (E) – sum of organic compounds; (F) – sum of cationic surfactants

4. Summary

The presented research results are basic overview on quality of sediments samples collected in the Klodnica River Catchment. Such physicochemical parameters like pH, concentration of inorganic ions, total organic carbon or total concentration of cationic surfactants can be used during evaluation of anthropogenic degradation of aquatic ecosystems.

Further analysis of collected samples should be conducted to compare different aspect of pollutants (PCB, metals, other surface active agents [10]-[12]) occurrence in water systems. After that obtained result should be analyzed with use of appropriated chemometric techniques to receive better view on degradation of the Klodnica River Catchment.

Improve of the knowledge in this area can prevent of uncontrolled the environment degradation. Exploring the migration pathways of pollutants and their effects on selected ecosystems should be one of the directions in science development.

5. Acknowledgement

Ewa Olkowska would like to thank the National Science Centre (Poland) for financial support (Decision no. DEC-2012/05/N/ST4/01995).

6. References

- [1] J. Nilin, L. B. Moreira, J. E. Aguiar, R. Marins, D. M. de Souza Abessa, T. M. da Cruz Lotufo, L. V. Costa-Lotufo. Sediment quality assessment in a tropical estuary: the case of Ceara River, Northeastern Brazil. *Mar. Environ. Res.* 2013, **91**: 89-96.
- [2] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten, B. Wehrli. The challenge of micropollutants in aquatic systems. *Science*, 2006, **313**: 1072-1077.
- [3] D. Fernandes, S. Pujol, E. Pérez-Albaladejo, R. Tauler, M. J. Bebianno, C. Porte. Characterization of the environmental quality of sediments from two estuarine systems based on different in-vitro bioassays. *Mar. Environ. Res.* 2013, doi: 10.1016/j.marenvres.2013.09.019.
- [4] A. Niedbala, M. Schaffer, T. Licha, K. Nödler, H. Bärnick, H. Ruppert, E. Worch, Influence of competing inorganic cations on the ion exchange equilibrium of the monovalent organic cation metoprolol on natural sediment. *Chemosphere* 2013, 90 (6) 1945-1951.
- [5] E. Olkowska, M. Ruman, A. Kowalska, Ż. Polkowska, Determination of surfactants in environmental samples – part I. Cationic compounds. *Ecol. Chem. Eng. S.* 2013, **20** (1): 69-77.

- [6] E. Olkowska, M. Ruman, Ź. Polkowska, Occurrence of surface active agents in the environment, *J. Anal. Methods Chem.* 2014: Article ID 769708.
- [7] M. Trochim, R. Machowski, M. Ruman, Przekształcenie rzeźby terenu i stosunków wodnych na obszarze zlewni Kłodnicy. In: R. Machowski, M. Ruman, (eds.) *Z badań nad wpływem antropopresji na środowisko*. 2006, Sosnowiec WNoZ, 2006 (In Polish).
- [8] M. Ruman, E. Olkowska, K. Koziół, D. Absalon, M. Matysik, Ź. Polkowska, Monitoring Strategy for Industrially Contaminated Rivers – Cost Reducing Practice Using Statistical Analysis, *J. Environ. Qual.* doi: 10.2134/jeq2013.06.0225.
- [9] E. Olkowska, Ź. Polkowska, J. Namieśnik, A solid phase extraction–ion chromatography with conductivity detection procedure for determining cationic surfactants in surface water samples, *Talanta* 2013, **116**: 210-221.
- [10] E. Olkowska, Ź. Polkowska, J. Namieśnik, Analytics of surfactants in the environment: problems and challenges, *Chem. Rev.* 2011, **111**: 5667-5700.
- [11] E. Olkowska, M. Ruman, A. Kowalska, Ź. Polkowska, Determination of surfactants in environmental samples – part II. Anionic compounds, *Ecol. Chem. Eng. S.* 2013, **20** (2): 331-342.
- [12] E. Olkowska, M. Ruman, A. Kowalska, Ź. Polkowska, Determination of surfactants in environmental samples – part III. Non-ionic compounds, *Ecol. Chem. Eng. S.* 2013, **20** (3): 449-461.