DOI: 10.21005/AAPZ2016.39.3.20

FOLIA POMERANAE UNIVERSITATIS TECHNOLOGIAE STETINENSIS
Folia Pomer. Univ. Technol. Stetin., Agric., Aliment., Pisc., Zootech. 2016, 328(39)3, 227–234

Kamil SZYDŁOWSKI, Michał STRĘK[1]

ANALYSIS OF FLUORIDE, DRY MATTER CONTENTS AND pH IN SEDIMENTS AND SURFACE WATER OF NOWOGARDZKIE LAKE

ANALIZA ZAWARTOŚCI FLUORKÓW, MATERII ORGANICZNEJ ORAZ pH W OSADACH DENNYCH I WODZIE POWIERZCHNIOWEJ JEZIORA NOWOGARDZKIEGO

Department of Ecology, Environmental Protection and Development, West Pomeranian University of Technology, Szczecin, Poland
[1]Department of Plant Physiology and Biochemistry, West Pomeranian University of Technology, Szczecin, Poland

Streszczenie. Określono wpływ formy użytkowania sąsiadującego terenu na zawartość fluorków w osadach dennych i wodzie. Dodatkowo wykonano analizę zawartości materii organicznej i pH w osadach i wodzie. Uzyskane wyniki odnoszą się do wody oraz osadów dennych z Jeziora Nowogardzkiego. Jezioro to położone jest częściowo w sąsiedztwie aglomeracji miejskiej, a częściowo w sąsiedztwie terenów użytkowanych rolniczo. Do badań pobrano 19 próbek osadów dennych oraz 5 próbek wód powierzchniowych. Wszystkie próbki pobrano w styczniu 2016 roku. Wyższe stężenie fluorków i materii organicznej zostało odnotowane w części zbliżonej do terenu rolniczego. Wyższe pH odnotowano w pobliżu terenu miejskiego. Wystąpiła również istotna dodatnia korelacja pomiędzy zawartością fluorków w osadach a ilością materii organicznej oraz ujemna korelacja pomiędzy pH osadów a zawartością materii organicznej.

Key words: agglomeration area, agricultural areas, bottom sediments, fluoride, surface water.
Słowa kluczowe: aglomeracja miejska, fluorki, obszary rolnicze, osady denne, wody powierzchniowe.

INTRODUCTION

Fluoride is widely spread in natural environment while it could be an important microelement and hazardous contaminant. It has the greatest electronegativity and reactivity of all elements from the periodic table (Cichocka 1996). The specific properties of fluoride can induce biological and ecological effects which have not been fully specified yet (Machoy-Mokrzyńska and Machoy 2006). This element gets into the environment as a result of natural processes. One of the most important processes is weathering of rocks from which fluoride is a component of. Other important sources are volcanic eruptions and forming of sea sprays (Camargo 2003). With the exception of these cases, other the existence of fluoride is a result of human action (Wędzisz 1994). The occurrence of fluoride in soil is connected with it existence in bedrock, while the content in the soil profile depends on the soil conditions, because depending on the type of soil, the element has a different accumulation capacity (Kabata-Pendias and Pendias 1999).

Corresponding author – Adres do korespondencji: Michał Stręk, Department of Plant Physiology and Biochemistry, West Pomeranian University of Technology, Szczecin, Juliusza Słowackiego 17, 71-434 Szczecin, Poland, e-mail: michal.strek@zut.edu.pl

Fluoride sorption in soil also depends on pH (Zhu et al. 2007). Some scientists consider that the contemporary non-natural changes of amount of F in the soil may be caused by phosphate fertilization (Kabata-Pendias and Pendias 1999; Kim et al. 2016). McGrath and Tunney (2010) studied the influence of phosphate fertilization on fluoride content in soil, and obtained results did not confirm the correlation between the occurrence of both elements, but they explained this by the low level of fluoride in the used fertilizer. But they admitted that fluoride deposition may occur in agricultural soil. From the solid phase the element can get into the water as an effect of weathering of rocks and leaching by atmospheric precipitation from the soil (Jarkowski and Grabecki 1995). Threat posed with cases of exceeded norms of concentration of fluoride in water is associated with water organisms, which uptake fluoride directly with water or food (Nell and Livanos 1988).

The size of the accumulation of element in living tissue depends on the concentration of its ions in the water, exposure time and temperature (Pillai and Mane 1985). Fluoride may also accumulate in the trophic level of a food chain in which it is toxic to aquatic organisms. High concentrations of hazardous substances existing in sediments can potentially threaten natural environment. (Sidoruk and Potasznik 2013). In bottom sediments, the organic matter is formed by sedimentation of remains of organisms, organic suspension and precipitation and coagulation of dissolved organic substances. Accumulated fluoride at the bottom of the lake sediments may be indigenous and also of allogeneic origin (Daniszewski 2012; Sidoruk and Potasznik 2013). The aim of study was to determine the impact of adjacent terrain usage on the fluoride content in sediments and water. Also there was made an examination of organic matter content and pH in sediments and water.

MATERIALS AND METHODS

The study applies to bottom sediments from Nowogardzkie Lake (Fig. 1). The water reservoir is located in West Pomeranian Voivodeship (53°39'58.55"N; 15° 5'56.49"E) more specifically partly within the Nowogard agglomeration and partly within farmlands. Total lake area is 103.78 ha, aerage depth is 5.2 m (max 10.9 m) and the total water volume is 5087.3 m^3 (Filipiak and Raczyński 2000). The object of the study has typical plant communities for such kind of reservoir i.e. common reed (*Phragmites australis* (Cav.) Trin. ex Steud), broadleaf cattail (*Typha latifolia* L.). Samples were collected using core sampler KC Denmark to obtain samples with intact structure in soft sediments. From each set of transect were taken two or three samples depending on the lake width. Sediments collection depth ranged from 0–0.3 m. The total number of samples collected was 19 from sediments and 5 from surface water. The sediment samples were prepared in accordance to procedures used in the soil science. The analyzes were conducted on the fraction with a particle diameter of less than 1 mm. Examination of the content of potentially available fluoride in bottom sediments was performed potentiometrically using ion-selective electrode pH-Ion Orion 920a based on the method by Ogoński and Samujło (1996) along with Nowak and Kuran's (2000) modification. The fluoride from sediments was extracted by 2M $HClO_4$. The fluoride content in water was determined based on the method described Durda et al. (1986). Stabilizing buffer TISAB III was added to all of the samples. The buffer addition keeps pH between 5.0 and 5.5 it allows to avoid the interference with OH^- ion.

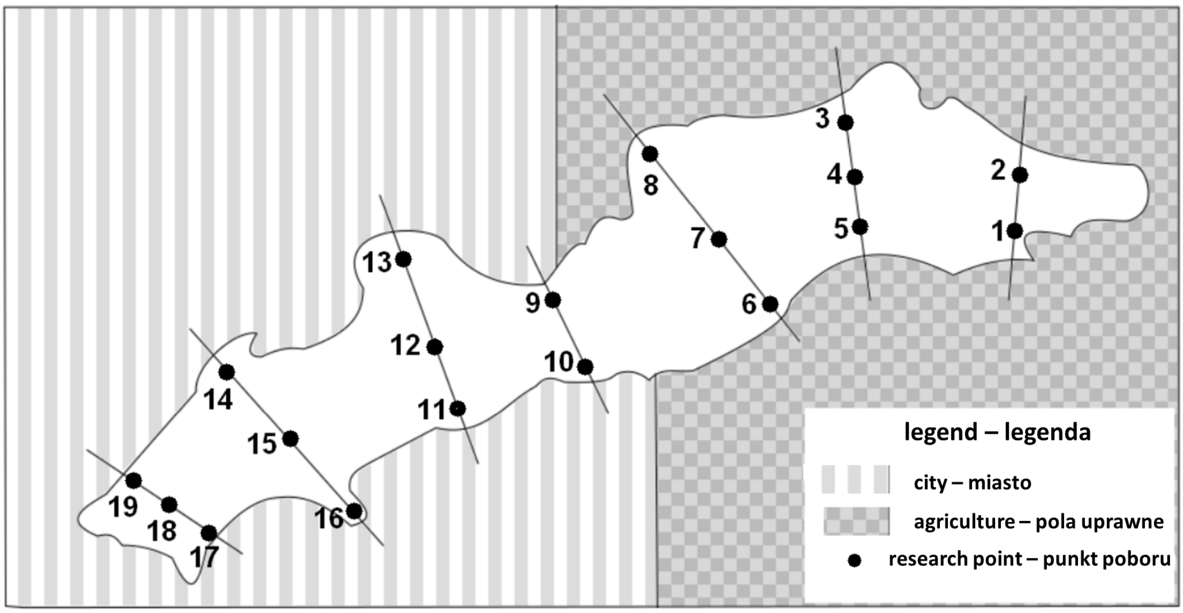

Fig. 1. The outline of the Nowogardzkie Lake with designated transects and areas of influence
Ryc. 1. Zarys Jeziora Nowogardzkiego z wyznaczonymi transektami oraz strefami oddziaływania

The organic matter content was calculated as a loss on ignition in 550ºC. The measurement of pH (exchangeable acidity) was conducted potentiometrically in a mixture of dry sediment and 1M KCl in the ratio 1 : 2.5. Obtained results were statistically analyzed using software Statistica 12.0. All results were verified with the Shapiro-Wilk test ($p \leq 0.05$), which confirmed the normality of distribution of figures. To determine significant differences between defined groups of measured points analyzes were performed with Tukey's test. Pearson correlation coefficient was used to determinate the relationship between the amount of organic matter and fluoride concentration. In the current study, all LSD and correlation coefficient (r) were expressed precisely in the text and were significant at $p \leq 0.05$.

RESULTS AND DISCUSSION

The fluoride content in the bottom sediments of the Lake Nowogardzkie ranged from 0 to 6.24 mg $F^- \cdot kg^{-1}$ d.m. Average concentration of the element for the whole object was 2.85 $F^- \cdot kg^{-1}$ d.m. (Table 1) while for each marked out area (city and agricultural) the mean values were 1.80 and 3.73 $F^- \cdot kg^{-1}$ d.m., respectively. The lowest fluoride content was in samples collected from points near the city beach, whereas the highest was in the middle of the agricultural part of the lake (research point 12) which is also the deepest place in the lake.

According to Szydłowski and Podlasińska (2016) accumulation of elements in the deepest points is a common phenomenon in case of ponds and it may be linked with sedimentation of the smallest fraction of allochtonic material. Research showed that at points located in the part of the lake adjacent to the municipal buildings, fluoride content in the sediments was 2.07 times lower than that in the adjacent agricultural area. It may be the result of number of agricultural treatments conducted, which include the use of chemical fertilizers. According to

Loganathan et al. (2001) increased amount of fluoride in the surface layer of the soil is related to phosphate fertilization. Kundu et al. (2009) argues that the fluoride content in the ground water from areas of intensive agricultural use significantly correlated with the amount of nitrogen fertilizers used. As a result of agricultural treatments and then leaching from the soil with ground water the element can get through to the lake water where is eventually deposited in the sediments. The mean value of fluoride concentration in water was 0.188 mg F · dm^{-3} and according to Telesiński et al. (2011), this amount of fluoride does not indicate contamination. Fluoride content in surface waters of Poland ranges between 0.01 and 100 mg F · dm^{-3} (Kabata-Pendias and Pendias 1999).

Table 1. Data obtained from analysis of investigated parameters of sediments
Tabela 1. Dane uzyskane z analizy oznaczanych parametrów osadów dennych

No. Lp.	Localization Lokalizacja	pH	Organic matter Materia organiczna [%]	Fluoride [mg · kg^{-1} d.m.] Fluorki [mg · kg^{-1} s.m.]
1	city – miasto	6.92	18.65	3.91
2	city – miasto	7.33	5.20	2.67
3	city – miasto	7.73	0.22	0.00
4	city – miasto	7.51	2.80	1.04
5	city – miasto	7.72	1.18	2.78
6	city – miasto	7.12	5.13	1.47
7	city – miasto	7.55	1.31	2.15
8	city – miasto	7.81	0.50	0.36
9	city – miasto	7.04	22.94	2.72
10	city – miasto	6.81	29.08	3.53
11	agriculture – pola uprawne	6.99	23.54	3.26
12	agriculture – pola uprawne	6.59	21.74	6.24
13	agriculture – pola uprawne	7.77	n.d.	4.09
14	agriculture – pola uprawne	6.59	37.63	2.30
15	agriculture – pola uprawne	7.34	0.59	3.86
16	agriculture – pola uprawne	7.39	39.13	4.30
17	agriculture – pola uprawne	6.87	17.90	2.89
18	agriculture – pola uprawne	7.08	12.31	3.70
19	agriculture – pola uprawne	6.89	31.45	4.16
Mean – Średnia		7.18	15.07	2.85
Standard deviation Odchylenie standardowe		0.38	13.57	1.52

ANOVA analysis also showed statistically significant differences (Tukey HSD test $p \leq 0.05$) in organic matter content, between points located adjacent to agricultural area, and the measuring points located in the urban vicinity (LSD = 0.011). The average content of organic matter in the Lake Nowogardzkie was 15.07%, with a standard deviation of 13.57% (Table 1). Higher average concentration of organic matter has been shown in Sidoruk and Potasznik's (2013) study performed on bottom sediments of the Lake Sunia, where the average organic matter content was 24.8%. Mean values of organic matter from each marked area were widely spread from 4.37% in the area surrounded by the city to 23.63% in the agricultural area. It is characteristic of glacial lakes, where the organic matter content ranges from 10% to 70% d.m. The lowest content of organic matter was found in the research point 3 (0.22%) in place of the shallow water. Small depth at this location explains the low organic matter content, as sediments deposited there are impoverished by the movement of the water that rinses the lighter particles and better oxygen conditions that cause higher mineralization. Higher content of the organic matter may affect intense primary production and supply of nutrients from the lake catchment intensively used for agriculture (Sidoruk and Potasznik 2013).

Table 2. Data obtained from analysis of investigated parameters of water
Tabela 2. Dane uzyskane z analizy oznaczanych parametrów wody powierzchniowej

No. Lp.	pH	Fluoride Fluorki [mg · kg^{-1}]
1	8.92	0.21
7	8.89	0.18
15	8.96	0.20
16	8.94	0.18
18	8.65	0.15
Mean Średnia	8.87	0.19
Standard deviation Odchylenie standardowe	0.13	0.02

Mean value of the lake sediments pH was 7.18 (Table 1). In sediments from each area, there was a significant difference between pH. The sediments from the part adjacent to the city have higher pH than those placed exactly near the agricultural area (7.46 and 7.03 respectively). Analysis of the surface water demonstrated alkaline properties; the mean pH value was 8.87 (Table 2) with standard deviation 0.13. Except for the change in pH caused by the lower concentration of organic matter an increase in pH value may be caused by the usage of building materials based on calcium in the city.

Table 3. Pearson correlation index for investigated parameters of sediments
Tabela 3. Współczynnik korelacji Pearsona dla oznaczanych parametrów osadów dennych

Variable	Fluoride Fluorki	pH	Organic matter Materia organiczna
Fluoride Fluorki		–	–
pH	–0.634*		–
Organic matter Materia organiczna	0.549*	–0.722*	

* Significnat at $p \leq 0.05$ – Statystycznie istotne przy $p \leq 0,05$.

The calculated Pearson correlation index ($p \leq 0.05$) (Table 3), show a negative correlation (–0.722) between pH and organic matter content and positive correlation between the content of organic matter and the fluoride concentration in the sediments (0.561). There was also negative correlation (–0.634) between fluoride concentration and pH. Research of other scientists showed that the amount of fluoride was in the relation with the content of organic matter in sediments and soil (Rao and Pal 1978, Pińskwar et al. 2000). It may be caused because sorption of fluoride occurs more intensively in acidic soils (Kabata-Pendias and Pendias 1999).

CONCLUSIONS

1. Closeness of areas used in different way have an impact on fluoride concentration, pH and organic matter content in sediments from Nowogardzkie Lake.
2. There was no correlation between fluoride concentration in water and sediments.
3. Concentration of fluoride in water and sediments of Nowogardzkie Lake do not indicate over normative contamination.

REFERENCES

Camargo J.A. 2003. Fluoride toxicity to aquatic organisms: a review. Chemosphere 50, 251–264.

Cichocka I. 1996. Fluor w środowisku leśnym. Poznań, W. „BAJT”. [in Polish]

Daniszewski P. 2012. Wartości stosunku C:N dla osadów dennych Jeziora Barlineckiego (wiosna, lato i jesień 2008 r.) [The C:N ratio of the analyzed of bottom sediments of the Barlinek Lake (spring, summer and autumn of 2008)]. Int. Lett. Chem. Phys. Astron. 2, 46–52. [in Polish]

Durda A., Machoy Z., Siwka W., Samujło D. 1986. Ocena stopnia przygotowania materiału badawczego do oznaczania fluorków [Assessment of the research material preparation degree to the fluoride determination]. Bromat. Chem. Toksykol. 19, 209–213. [in Polish]

Filipiak J., Raczyński M. 2000. Jeziora zachodniopomorskie (zarys faktografii). Szczecin, Wydaw. AR, 255. [in Polish]

Kabata-Pendias A., Pendias H. 1999. Biogeochemia pierwiastków śladowych. Warszawa, PWN. [in Polish]

Kim N.D., Taylor M.D., Drewry J.J. 2016. Anthropogenic fluorine accumulation in the Waikato and Bay of Plenty regions of New Zealand: comparison of field data with projections. Environ. Earth Sci. 75, 147. DOI: 10.1007/s12665-015-4897-2

Kundu M.C., Mandal B., Hazra G.C. 2009. Nitrate and fluoride contamination in groundwater of intensively managed agroecosystems: a functional relationship. Sci. Total. Environ. 407, 2771–2782.

Loganathan P., Hedley M.J., Wallace G.C., Roberts A.H.C. 2001. Fluoride accumulation in pasture forages and soils following long-term applications of phosphorus fertilizers. Environ. Pollut. 115, 275–282.

Machoy-Mokrzyńska A., Machoy Z. 2006. Aktualne kierunki badań nad fluorem [Current trends in fluorine research]. Ann. Acad. Med. Stetin. 52, Suppl. 1, 73–77. [in Polish]

McGrath, D., Tunney, H. 2010. Accumulation of cadmium, fluorine, magnesium, and zinc in soil after application of phosphate fertilizer for 31 years in a grazing trial. J. Plant Nutr. Soil Sci. 173(4), 548–553

Nell J.A., Livanos G. 1988. Effects of fluoride concentration in seawater on growth and fluoride accumulation by Sydney rock oyster (*Saccostrea commercialis*) and flat oyster (*Ostrea angasi*) spat. Water Res. 22, 749–753.

Nowak J., Kuran B. 2000. Dynamika przemian fluoru w glebie z form rozpuszczalnych do nierozpuszczalnych w wodzie [The dynamics of fluorine transformations in soil from water soluble to insoluble forms]. Rocz. Glebozn. 51(2), 125–133. [in Polish]

Ogoński T., Samujło D. 1996. Metody stosowane w analityce fluoru (in: Analityka związków fluoru. Sympozjum Metabolizm fluoru), Szczecin 26, 27.04.1996, 11–14. [in Polish]

Pillai K.S., Mane U.H. 1985. Effect of fluoride effluent on fry *Catla catla* (Hamilton). Fluoride 18, 104–110.

Pińskwar P., Jezierska-Madziar M., Furmaniak P. 2000. Fluoride compounds content in the water and bottom sediments in the Warta River old riverbed in Luboń. Folia Univ. Agric. Stetin., Ser. Piscaria 214(27), 159–172.

Rao D.N., Pal D. 1978. Effect of fluoride pollution on the organic matter content of soil. Plant Soil 49, 653–656.

Sidoruk M., Potasznik A. 2013. Ocena stanu zanieczyszczenia ołowiem, cynkiem i chromem osadów dennych jeziora Sunia [Assessment of lead, zinc and chromium contamination of bottom sediments in lake Sunia]. Proc. ECOpole 7(2), 713–720. [in Polish]

Szydłowski K., Podlasińska J. 2016. Charakterystyka osadów dennych oczek wodnych [Characteristics of sludge bottom mesh]. Ecol. Eng. 47, 40–46. DOI: 10.12912/23920629/62845. [in Polish]

Telesiński A., Śnioszek M., Środa M. 2011. Akumulacja fluorków w wybranych gatunkach hydromakrofitów w zależności od ich koncentracji w wodzie i osadach dennych rzeki Gunica [Fluoride accumulation in chosen hydromacrophytes species depending on their content in water and sediments of Gunica river]. Ochr. Środ. Zas. Natur. 49, 345–353. [in Polish]

Wędzisz A. 1994. Fluor – środowisko – żywność [Fluorine – environment – food]. Bromat. Chem. Toksykol. 27, 347–352. [in Polish]

Zhu M.-X., Ding K.-Y., Jiang X., Wang H.-H. 2007. Investigation on co-sorption and desorption of fluoride and phosphate in a red soil of China. Water Air Soil Pollut. 183, 455–465. DOI: 10.1007/s11270-007-9394-0.

Abstract. The aim of study was to determine the impact of adjacent terrain usage on the fluoride content in sediments and others important ecological indicators. All of results applies to bottom sediments and surface water from Nowogardzkie Lake. The lake is partly within the Nowogard agglomeration and partly within farmlands. The total number of collected samples was 19 from sediments and 5 from surface water. The all samples were collected in January 2016. Higher concentrations of fluoride and organic matter content were recorded in agricultural adjacent area and pH of sediments was higher in city area. There was correlation between fluoride content in sediments and organic matter content. There was also negative correlation betwen pH in sediments and organic matter content.