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ZINC, COPPER AND NICKEL IN SEQUENTIAL EXTRACTED FRACTIONS IN BOTTOM SEDIMENTS

CYNK, MIEDŹ I NIKIEL W SEKWENCYJNIE WYDZIELONYCH FRAKCJACH Z OSADÓW DENNYCH

Abstract: The total content of Zn, Cu, Ni, and their contribution in exchangeable (F1), reducible (F2), oxidizable (F3), and residual (F4) fractions separated by the sequential extraction procedure according to The European Union's Standards, Measurements, and Testing program (formerly BCR), in bottom sediments were determined. Samples were collected from bottom sediments surface layer (0–10 cm) of the "Row Strzala" canal that disposes reclaimed wastewaters from municipal sewage treatment plant in Siedlce and storm sewage system, to Liwiec river, as well as in the river, upstream and downstream of the canal estuary, located on the Siedlce Upland, in the eastern part of Mazovia province. The mean contents of tested heavy metals in surface layers of bottom sediments can be lined up in following decreasing sequence [$mg \cdot kg^{-1}$]: Zn (69.1) > Cu (5.81) > Ni (3.95). Higher total contents of Zn, Cu, and Ni were recorded in bottom sediments from canal rather than river. More studied metals were recorded in material collected from points near sewage treatment plant, while less at the point localized above its estuary to Liwiec river. Sediments from studied flows are counted to the 1st class – not contaminated sediments. The mean percentage contribution of Zn, Cu, and Ni in separated fractions, in relation to their total contents, can be arranged in the following decreasing series: for Zn: F2 (53.6) > F3 (21.0) > F4 (15.3) > F1 (10.2); for Cu: F3 (50.4) > F4 (25.7) > F2 (15.0) > F1 (8.90); for Ni: F4 (39.6) > F3 (26.6) > F2 (20.2) > F1 (13.6). Mobility of metals in exchangeable fraction (F1) in the investigated sediments can be lined up in following decreasing sequence Ni > Zn > Cu. Statistical processing revealed significant influence of selected properties of studied bottom sediments (sediments reaction, content of organic carbon compounds, value of cation exchange capacity, clay fraction – ∅ < 0.002 mm) on zinc, copper and nickel speciation.

Keywords: bottom sediments, fraction of Zn, Cu, Ni, "Row Strzala" canal, Liwiec river

Bottom sediments are an important part of the aquatic environment. They form a habitat for plants and animals which is rich in nutrients and which plays an important role in the regulation of matter and energy circulation in the environment. Sediments in

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the surface water are formed as a result of sedimentation on the bottoms of watercourses of allochthonous material originating outside the sedimentation area (gravel, sand, silt, mineral and organic suspensions) and autochthonous material formed in the sedimentation area (depositing organic and inorganic substances, as well as decaying plant and animals remnants). Heavy metals are commonly regarded as particularly noxious and hazardous to the natural environment, frequently causing its pollution. When introduced to surface waters, they accumulate in bottom deposits, where their content is higher than in water. The intensity of element migration in the ecosystem is affected by geochemical, physicochemical, climatic and biological factors. The chemical composition of bottom sediments in watercourses depends on the geological structure of the drainage basin, the natural of land use around it and pollutants which enter surface waters (industrial and household sewage and surface runoff from agricultural land). The metal content in bottom deposits is an important indicator of the geochemical quality of an aquatic ecosystem and it provides important information on the anthropopressure on aquatic environment [1–6].

The total content of heavy metals in bottom deposits comprises their various fractions (species) with varying properties which take part in many processes in the environment, typical of a given form. The properties of deposits, such as pH, red-ox potential, sorption capacity, type and amount of organic matter, content of carbonates and iron and manganese compounds affect the occurrence of metals as different species. The mobility of heavy metals accumulated in deposits and their toxicity to living organisms depends on the presence of those metals in potentially bioavailable forms whose quantitative and qualitative isolation is enabled by speciation analysis. Methods of sequential extraction provide important information on hazards to ecosystems from deposited heavy metals, which may become secondary sources of pollution as a result of chemical and biochemical processes, circulating within systems consisting of a bottom deposit, water, living organisms and a water course environment [6–12].

The aim of the study was to evaluate the content of zinc, copper and nickel and their amounts in isolated fractions of bottom sediments in the "Row Strzala" canal, channelling off post-treatment waters from the communal wastewater treatment plant in Siedlce to the Liwiec river, as well as in the river, upstream and downstream of the canal estuary.

Material and methods

The studied object comprised of bottom sediments from two water flows (the "Row Strzala" canal and Liwiec river) localized within the boundaries of Strzala and Chodow villages near Siedlce in eastern part of Mazovia region (Fig. 1). The "Row Strzala" is a canal that disposes reclaimed waters from municipal sewage treatment plant in Siedlce and storm sewage system to Liwiec river. Liwiec river is a right tributary of Bug river and one of the larger rivers on the South-Podlasie Lowland, that in its upper section flows through the Siedlce Upland. On studied area, these flows pass through agricultural areas (arable lands, meadows, pastures) built of sandy forms of water and glacial accumulation as well as shallow organic sediments (peats and organic silts) [13].

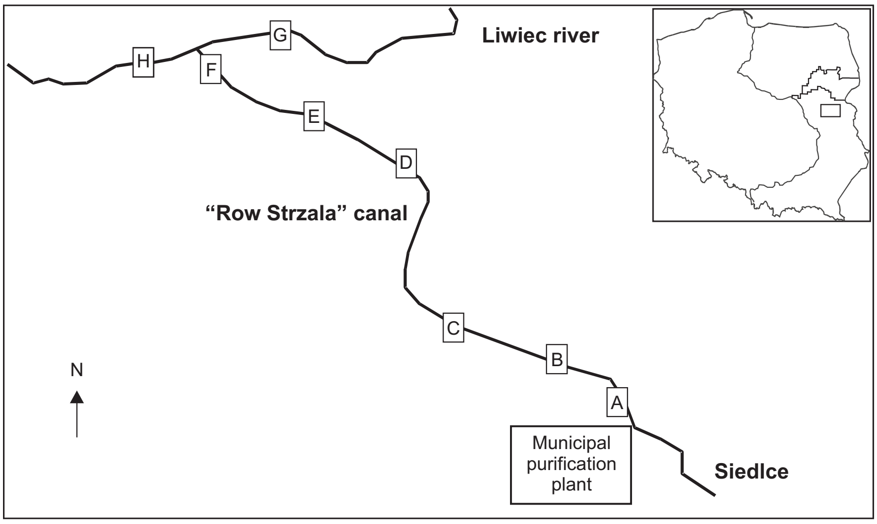

Fig. 1. The location of bottom sediments sampling sites in canal of the "Row Strzala" canal (A–F) and Liwiec river (G–H)

Samples were collected in polyethylene bags using a plastic scoop from surface layer of sediments (0–10 cm) at 8 representative points (three samples were taken from each point to obtain a representative sample on 10 m distance): 6 – in the "Row Strzala" bed (A, B, C, D, E, F), on distance of about 2 km between sewage treatment plant (N: $52^o11'37''$, E: $22^o15'24''$) and Liwiec river (N: $52^o12'33''$, E: $22^o13'56''$), and 2 – in Liwiec river bed, upstream – site G (N: $52^o12'37''$, E: $22^o11'14''$) and downstream – site H (N: $52^o12'30''$, E: $22^o13'42''$) of the canal estuary.

The bottom sediments samples air dried, sieved through a 2 mm mesh and then the following properties were determined: granulometric composition according to the Polish Soil Science Society [14] – by the *areometric* method, pH in 1 mol KCl · dm^{-3} – *potentiometrically*, the amount of organic carbon (C_{org}) – by the *oxidation-reduction* method [15]. *Cation exchange capacity* (CEC) values and the *index of soil saturation with base cations* (V) were calculated on the basis of *hydrolytic acidity* (HA) and the *sum of base exchangeable cations* determined by Kappen's method.

The total content of zinc (Zn_{tot}), copper (Cu_{tot}) and nickel (Ni_{tot}) were assessed by ICP-AES method (Optima 3200 RL, Perkin-Elmer) after homogenization bottom sediments samples in an agate mill and mineralization in mixture of concentrated HCl and HNO_3 (3:1) in a microwave system (Multiwave, Anton Paar).

The fractions of zinc, copper and nickel were determined by the *sequential extraction procedure* (in samples homogenized in an agate mill) proposed by The European Union's Standards, Measurements and Testing program (SM&T, formerly BCR) [7], in which four fractions were separated: F1 – *exchangeable*; F2 – *reducible*; F3 – *oxidizable*; F4 – *residual* (post-extractions remaining) (Table 1). The content of zinc, copper and nickel in particular fractions was determined by ICP-AES method. The percentage contribution of separated four fractions of Zn, Cu and Ni in relation to their total content were calculated. The suitability of the sequential extraction method was compared with that of the external standard method. The analysis also covered control samples, for which the identical analytical procedure was applied as for the study material. The analysis was conducted in triplicate and the tables show the average values.

Table 1

Reagents and reaction conditions of the sequential extraction procedure used in the investigated bottom sediments of the "Row Strzala" canal and Liwiec river

Fraction	Nominal target phase	Chemical reagents and conditions
F1 Exchangeable	Water and acid soluble species, cation exchange sites; specifically adsorbed ions and bound by weak electrostatic interactions	0.11 mol $CH_3COOH \cdot dm^{-3}$; pH = 3; shake for 16 h at 20 °C
F2 Reducible	Bound to iron and manganese oxyhydroxides	0.5 mol $NH_2OH\text{-}HCl \cdot dm^{-3}$; pH = 2; shake for 16 h at 20 °C
F3 Oxidizable	Bound to organic matter and sulfides	8.8 mol $H_2O_2 \cdot dm^{-3}$ (pH = 2–3); heat to 85 °C for 2 h (repeat again), and followed by 1 mol $CH_3COONH_4 \cdot dm^{-3}$ (pH = 2), and shake for 16 h at 20 °C
F4 Residual (post-extraction remaining)	Strongly associated to crystalline structures of minerals	Calculated as the difference between the total content of a particular heavy metals and the sum of their fraction: F1, F2, and F3, extracted during the previous steps

The relationships between Zn, Cu and Ni content in each fraction and selected properties of the bottom deposits under study were evaluated with linear correlation at two levels of significance $\alpha = 0.05$ and $\alpha = 0.01$.

Results and discussion

The bottom sediments under study were classified as weakly loamy sand and loose sand, whose selected physical, physicochemical and chemical properties are presented in Table 2. The pH values of the deposits was weakly acidic to alkaline (6.52–7.65) and their hydrolytic acidity (HA): 5.0–8.6 mmol(+) $\cdot$ kg^{-1}; the *sum of base exchangeable cations* (BEC): 49.0–272.0 mmol(+) $\cdot$ kg^{-1}, cation exchange capacity (CEC): 57.6–272.0 mmol(+) $\cdot$ kg^{-1}, the index of soil saturation with base cations (V): 85.1–98.1 % and *organic carbon content* (C_{org}): 0.68–19.6 g $\cdot$ kg^{-1}. The highest values of BEC, CEC and V and the lowest value of HA were found in samples with the highest organic carbon content (sites A, B and G). The pH values, the sum of base exchangeable cations, cation exchange capacity and the index of soil saturation with base cations as well as organic carbon and *clay fraction* (∅ < 0.002 mm) content in deposits in the "Row Strzala" were found to decrease, while the value of hydrolytic acidity was found to increase with the distance from the wastewater treatment plant. Deposits in the Liwiec river were found to contain a higher content of C_{org} (8.59 g $\cdot$ kg^{-1}) and the values of BEC (141.3 mmol(+) · kg^{-1}), CEC (147.0 mmol(+) · kg^{-1}) and V (95.4 %) were also higher than those in the "Row Strzala" (7.13; 124.8; 132.0 and 91.8, respectively).

Table 2

The total content [mg · kg^{-1}] of Zn, Cu, Ni, and some properties of investigated bottom sediments of the "Row Strzala" canal (A–F), and Liwiec river (G–H)

Some properties	Sampling sites							
	A	B	C	D	E	F	G	H
Sand 2–0.5*	90	89	93	93	94	94	92	94
Silt 0.5–0.002*	7	7	4	5	4	4	6	3
Clay < 0.002*	3	4	3	2	2	2	2	3
Granulometric group	ps	ps	pl	pl	pl	pl	pl	pl
pH_{KCl}	6.86	7.22	6.85	6.64	6.63	6.52	7.65	6.88
HA [mmol(+) · kg^{-1}]	6.5	5.3	6.9	7.8	8.0	8.6	5.0	6.6
BEC [mmol(+) · kg^{-1}]	225.5	266.7	73.4	69.1	65.1	49.0	190.0	92.5
CEC [mmol(+) · kg^{-1}]	232.0	272.0	80.3	76.9	73.1	57.6	195.0	99.1
V [%]	97.2	98.1	91.4	89.9	89.1	85.1	97.4	93.3
C_{org} [g · kg^{-1}]	18.3	19.6	1.65	1.31	1.25	0.68	14.9	2.27
Zn_{tot} [mg · kg^{-1}]	115.3	124.1	36.0	55.1	57.4	72.1	27.1	65.4
Cu_{tot} [mg · kg^{-1}]	9.11	11.3	5.15	4.91	4.32	4.19	3.10	4.38
Ni_{tot} [mg · kg^{-1}]	5.22	6.08	4.02	3.49	3.30	3.18	2.26	3.38

* % fraction of diameter in mm; ps – weakly loamy sand, pl – loose sand; HA – hydrolitic acidity; BEC – the sum of base exchangeable cations; CEC – cation exchenge capacity; V – the index of soil saturation with base cations; Zn_{tot}, Cu_{tot}, Ni_{tot} – total content of Zn, Cu, Ni.

Licznar et al [4] and Skorbilowicz and Wiater [16] emphasised that the content of organic carbon and the granulometric composition of bottom deposits are affected by the soil in the drainage basin and they arise from transport and sedimentation of particles carried by water current. Accumulation of organic matter takes place in slowly flowing water and during periods of stagnation and affects the sorption properties of the deposits. High sorption capacity and saturation of the sorption complex with base cations have a beneficial effect on the buffer properties of bottom deposits which, in turn, affect sorption and desorption of heavy metals in an aquatic environment [4, 17].

The surface layer of the sediments (0–10 cm) was found to contain varied amounts of heavy metals whose decreasing average content [mg · kg^{-1}] is shown in the following order: Zn (69.1) > Cu (5.81) > Ni (3.95). The difference may be a result of the geochemical nature of an element and the properties of bottom deposits (pH, cation exchange capacity, organic carbon content and clay fraction – ∅ < 0.002 mm) [1]. The metal content was higher in the bottom deposits of the "Row Strzala" canal (average values: Zn – 76.7 mg · kg^{-1}, Cu – 6.50 mg · kg^{-1} and Ni – 4.33 mg · kg^{-1}) than in the Liwiec (46.3; 3.74 and 2.82 mg · kg^{-1}, respectively). The highest concentrations of the metals under study were found in the material taken from the canal near the wastewater plant (sites A and B) and the lowest were at a site situated upstream of its estuary to the

Liwiec (site G) (Zn – 27.1 mg · kg^{-1}; Cu – 3.10 mg · kg^{-1} and Ni – 2.26 mg · kg^{-1}). Higher concentrations of zinc (65.4 mg · kg^{-1}), copper (4.38 mg · kg^{-1}) and nickel (3.38 mg · kg^{-1}) in the bottom deposits of the Liwiec, taken at site H situated downstream of the canal estuary, resulted from their higher content in the deposits in the "Row Strzala" canal (Table 2).

The total content of zinc, copper and nickel at sites A and B and the content of zinc at sites D, E, F, H in the bottom deposits exceeded the values for the geochemical background for bottom sediments in Polish rivers (Zn 48.0 mg · kg^{-1}, Cu – 6.0 mg · kg^{-1}, Ni – 5.0 mg · kg^{-1}) [18]. According to the classification of water deposits proposed by Bojakowska [2], the deposits were included in class I – uncontaminated deposits, with the total content of Zn, Cu and Ni not exceeding the *lower potential toxicity threshold* (TEL) and not posing any threat to living organisms.

The highest content of heavy metals is found in bottom deposits near the source of contamination, but the elements can be transported downstream to lower sections of rivers with silt fractions and organic matter of deposits [1, 2, 19]. Skorbilowicz [3], Licznar et al [4], Skorbilowicz and Wiater [16, 20] and Ziola et al [21] examined bottom deposits in rivers and canals flowing through agricultural lands and found them to contain varied amounts of zinc (9.30–75.4 mg · kg^{-1}), copper (0.90–38.2 mg · kg^{-1}) and nickel (0.30–16.8 mg · kg^{-1}). Much more of those metals accumulate in bottom deposits in areas with high anthropopressure (industrial and communal sewage, mining industry, metallurgy, waste dumpsites) [9, 11, 19, 22–24]. Bottom sediments in Polish rivers, examined in the years 2003–2005 as part of the National Environment Monitoring programme, were found to contain varied amounts of Zn (7–12.000 mg · kg^{-1}), Cu (1–375 mg · kg^{-1}) and Ni (1–76 mg · kg^{-1}), with about 50 % of the deposits containing less than 125 mg · kg^{-1} of zinc and about 40 % of them containing less than 10 mg · kg^{-1} of copper and nickel [5].

The bottom deposits under analysis contained varied amounts of zinc, copper and nickel in four fractions, isolated sequentially by the BCR method (Table 3). The average percentage of the metals in the fractions is shown in the following sequences of decreasing percentage values of their total content: Zn – F2 (53.6) > F3 (21.0) > F4 (15.3) > F1 (10.2); Cu – F3 (50.4) > F4 (25.7) > F2 (15.0) > F1 (8.90); Ni – F4 (39.6) > F3 (26.6) > F2 (20.2) > F1 (13.6). Similar sequences for Zn, Cu and Ni fractions in deposits from different watercourses have been presented by Mossop and Davidson [8], Glosinska et al [9], Morillo et al [11], Purushothaman and Chakrapani [19], Karczewska et al [24], Stephens et al [25], Tuzen [26], Dabrowska [27], Sokolova et al [28], Rodrigues and Formoso [29].

The highest concentration of zinc in bottom deposits are usually found as combinations with Fe and Mn compounds (reducible fraction – F2), 20–75 % on average; copper is usually found in combinations with organic matter and sulphides (oxidizable fraction – F3), 30–59 % on average, while nickel forms stable combinations of the residual fraction (F4) – up to 90 % [1, 9, 11, 19, 22, 24–27, 29]. The average content of Zn, Cu and Ni in the most mobile and the most bioavailable exchangeable fraction (F1) in the bottom deposits under study (and, consequently, their capability of migrating to the water of the "Row Strzala" canal and the Liwiec) was the following: Ni (13.6 %) > Zn

(10.2 %) > Cu (8.90 %). A similar sequence in bottom deposits of the Kozlowa Gora water body was found by Dabrowska [27], while the proportion of Zn, Cu and Ni in mobile fractions of the Middle Odra river sediments was the following: Ni (12–59 %) > Cu (9–50 %) > Zn (7–36 %) [9].

Table 3

The percentage contribution of Zn, Cu, Ni fractions in the investigated bottom sediments of the "Row Strzala" canal (A–F) and Liwiec river (G–H)

Fractions	Sampling sites								Mean
	A	B	C	D	E	F	G	H	
Zn									
F1	5.28	5.64	10.9	11.3	12.7	13.0	8.74	13.7	10.2
F2	51.5	50.1	55.1	54.7	54.5	56.7	52.0	53.9	53.6
F3	32.5	32.0	18.1	17.6	16.2	13.4	23.5	14.7	21.0
F4	10.7	12.3	15.9	16.3	16.7	16.9	15.8	17.7	15.3
Cu									
F1	5.60	5.13	7.57	8.55	11.1	12.4	8.06	12.8	8.90
F2	9.11	10.3	12.6	16.9	20.1	22.0	13.5	15.5	15.0
F3	68.9	73.0	49.1	43.3	37.2	33.0	60.6	37.9	50.4
F4	16.4	11.6	30.7	31.2	31.6	32.6	17.7	33.8	25.7
Ni									
F1	13.2	10.5	13.0	14.5	15.7	15.9	10.3	15.6	13.6
F2	19.0	16.0	21.3	21.7	21.9	22.2	19.6	20.2	20.2
F3	29.9	34.5	27.1	24.1	22.4	21.5	30.7	22.5	26.6
F4	37.9	38.9	38.5	39.8	40.0	40.4	39.4	41.7	39.6

Fraction: F1 – exchangeable, F2 – reducible (bound to Fe-Mn oxide), F3 – oxidizable (bound to organic matter), F4 – residual.

The proportion of zinc, copper and nickel in the exchangeable (F1), reducible (F2) and residual (F4) fraction in the "Row Strzala" canal sediments increased with the distance from the wastewater treatment plant, reaching the maximum values before the estuary to the Liwiec, at site F. The percentage of the metals in the oxidizable fraction (F3) decreased with increasing distance from the wastewater treatment plant, reaching the minimum values at site F (Table 3). The bottom deposits taken in the Liwiec downstream of the canal estuary (site H), were found to contain higher proportion of Zn, Cu and Ni in fractions F1, F2 and F4 and their lower proportion in fraction F3 as compared with the site upstream of the canal estuary (G) (Table 3). The mobility of heavy metals contained in the exchangeable fraction (F1) increases at decreasing pH values and in variable red-ox conditions, especially in sandy formations, which poses a real and potential hazard to aquatic ecosystems and biotic links of the food chain [11, 19, 25]. When the pH is close to alkaline values, solubility and mobility of organic compounds of heavy metals increases, and their high percentage in fraction F1 in aquatic environment can be toxic to plants and animals [1, 6, 24]. Large amounts of metals in biologically inactive and stable mineral combinations of the residual fraction

(F4) and small amounts in the bioavailable and mobile exchangeable fraction (F1) are typical of uncontaminated deposits [11, 19, 22, 25, 26, 29].

Correlations between most of the examined parameters were found to exist in the bottom sediments under study (Table 4). Statistical analysis showed a significant negative effect of total content of zinc (Zn_{tot}), copper (Cu_{tot}) and nickel (Ni_{tot}), total organic carbon (C_{org}), cation exchange capacity (CEC) on the percentage of the metals in the exchangeable fraction (F1), with the strongest link existing for nickel (from r = –0.753 to r = –0.830). The content of the analysed metals in the reducible fraction (F2) correlated with the cation exchange capacity (Zn – r = 0.936; Cu – r = 0.853; Ni – r = 0.927; at α = 0.01). A highly significant positive effect of the C_{org} content and CEC value on the amount of Zn, Cu and Ni in the oxidizable (F3) and residual (F4) fraction was observed, with the strongest relationships existing for copper (r = 0.966 and r = 0.992 for F3 and r = 0.976 and r = 0.966 for F4). Moreover, a significant relationship was observed in the analysed deposits between the amount of the clay fraction (∅ < 0.002 mm) and the percentage of zinc in fraction F4 (r = 0.742) and copper and nickel in fraction F2 (r = 0.732 and 0.806, respectively). The pH values of water deposits significantly correlated with the percentage of the metals in fraction F3 (Zn – r = 0.831; Cu – r = 0.798; Ni – r = 0.776).

Table 4

The correlation coefficients between the Zn, Cu, Ni fractions and some properties of the investigated bottom sediments

Zinc									
	F1	F2	F3	F4	Zn_{tot}	pH_{KCl}	C_{org}	CEC	∅ < 0.002
F1	x	–0.540	–0.832*	0.829*	–0.714*	–0.529	–0.742*	–0.781*	–0.563
F2		x	–0.767*	–0.654	0.776*	–0.382	0.308	0.936**	0.568
F3			x	–0.843**	0.458	0.831*	0.954**	0.937**	0.437
F4				x	0.621	–0.283	0.842**	0.936**	0.742*
Copper									
	F1	F2	F3	F4	Cu_{tot}	pH_{KCl}	C_{org}	CEC	∅ < 0.002
F1	x	0.819*	–0.825*	0.658	–0.733*	0.470	–0.780*	–0.806*	–0.544
F2		x	–0.826*	0.640	–0.651	–0.580	–0.688	0.853**	0.732*
F3			x	–0.957**	0.734*	0.798*	0.966**	0.992**	0.578
F4				x	0.647	–0.684	0.976**	0.966**	–0.448
Nickel									
	F1	F2	F3	F4	Ni_{tot}	pH_{KCl}	C_{org}	CEC	∅ < 0.002
F1	x	0.748*	–0.821*	0.260	–0.753*	–0.680	–0.809*	–0.830*	–0.437
F2		x	–0.807*	–0.118	0.255	–0.639	–0.683	0.927**	0.806*
F3			x	–0.856**	0.463	0.776*	0.913**	0.912**	0.578
F4				x	–0.069	–0.042	0.842**	0.876**	0.120

Significance at: α = 0.05* (r = 0.707); α = 0.01** (r = 0.834).
Fraction: F1 – exchangeable, F2 – reducible (bound to Fe-Mn oxide), F3 – oxidizable (bound to organic matter), F4 – residual.

Glosinska et al [9] examined bottom deposits and found a significant effect of the total content of zinc, copper and nickel on their content in fractions F1, F2, F3 i F4. Speciation of Zn, Cu and Ni in aquatic environment depends largely on the pH value and cation exchange capacity and organic carbon and clay fraction content [1, 11, 19, 25, 26].

Conclusions

1. Bottom sediments in the "Row Strzala" canal and in the Liwiec river downstream and upstream of the canal estuary were found to contain varied concentrations of zinc, copper and nickel and the content was higher in the canal deposits than the river deposits. The deposits under study were included in class I for metal content – uncontaminated deposits.

2. The average percentage of the analysed metals can be shown in the following sequence in decreasing order: for Zn F2 > F3 > F4 > F1; for Cu F3 > F4 > F2 > F1; for Ni F4 > F3 > F2 > F1.

3. The mobility of the metals in the deposits of the watercourses can be shown in the decreasing sequence of their content on the exchangeable fraction (F1): Ni > Zn > Cu.

4. As the distance from the wastewater treatment plant grew, the content of the metals under study in the exchangeable fraction (F1), reducible fraction (F2) and residual fraction (F4) of the bottom deposits of the "Row Strzala" canal increased and it decreased in the oxidizable fraction (F3).

5. The bottom deposits in the Liwiec, downstream of the canal estuary, were found to contain higher proportion of the metals under study in fractions F1, F2 and F4 and their lower content in fraction F3.

6. Statistical analysis has shown a significant effect of selected properties of the sediments (pH, C_{org}, CEC, clay fraction) on the speciation of zinc, copper and nickel.

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CYNK, MIEDŹ I NIKIEL W SEKWENCYJNIE WYDZIELONYCH FRAKCJACH Z OSADÓW DENNYCH

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Abstrakt: Badano zawartość ogólną cynku, miedzi i niklu oraz ich udział we frakcji wymiennej (F1), redukowalnej (F2), utlenialnej (F3) oraz rezydualnej (F4), wydzielonych według sekwencyjnej procedury rekomendowanej przez The European Union's Standards, Measurements, and Testing program (dawniej BCR), w osadach dennych kanału „Rów Strzała", odprowadzającego wody pościekowe z oczyszczalni ścieków komunalnych w Siedlcach i kanalizacji burzowej do rzeki Liwiec, a także w tej rzece, przed i za ujściem kanału, w miejscowościach Strzała i Chodów, na Wysoczyźnie Siedleckiej, we wschodniej części województwa mazowieckiego. W powierzchniowej warstwie (0–10 cm) badanych osadów stwierdzono zróżnicowaną zawartość metali ciężkich, których malejące średnie wartości ($mg \cdot kg^{-1}$) przedstawiono w następującym szeregu: Zn (69,1) > Cu (5,81) > Ni (3,95). Zwartość ogólna Zn, Cu i Ni była większa w osadach dennych kanału niż rzeki. Najwięcej badanych metali stwierdzono w materiale pobranym z kanału w pobliżu oczyszczalni ścieków, a najmniej – w miejscu położonym powyżej jego ujścia do rzeki Liwiec. Osady badanych cieków zaliczono pod względem zawartości tych metali do klasy I – osadów nie zanieczyszczonych. Średni procentowy udział analizowanych metali w wydzielonych frakcjach, w stosunku do ich zawartości ogólnej, układał się w następujących szeregach malejących wartości dla Zn – F2 (53,6) > F3 (21,0) > F4 (15,3) > F1 (10,2); dla Cu – F3 (50,4) > F4 (25,7) > F2 (15,0) > F1 (8,90); dla Ni – F4 (39,6) > F3 (26,6) > F2 (20,2) > F1 (13,6). Mobilność metali w osadach badanych cieków wodnych układała się w szeregu ich malejącego średniego udziału we frakcji wymiennej (F1) następująco: Ni > Zn > Cu. Obliczenia statystyczne wykazały, że zawartość cynku, miedzi i niklu w wydzielonych frakcjach jest na ogół znacząco zależna między tymi metalami oraz wybranymi właściwościami badanych osadów dennych (pH, zawartość węgla związków organicznych, kationowa pojemność sorpcyjna, frakcja iłowa – ∅ < 0,002 mm).

Słowa kluczowe: osady denne, frakcje Zn, Cu, Ni, kanał Rów Strzała, rzeka Liwiec