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QUANTITATIVE AND QUALITATIVE NUMERICAL ANALYSIS OF OPERATIONAL CONDITIONS OF STORM WATER SYSTEM

IŁOŚCIOWA I JAKOŚCIOWA ANALIZA NUMERYCZNA FUNKCJONOWANIA SIECI KANALIZACJI DESZCZOWEJ

Abstract: Operation of storm water systems in urbanized catchments, affected by increased size of drained area and its relative surface sealing, significant variability of rainfall events and increased usage of transport vehicles is connected to changes of sewage flow, pollutants concentrations and loads entering the sewage receiver. Thus, the application of numerical modeling to multi-variant analyses of storm water systems operation and its influence on the natural environment is reasonable and becomes a standard procedure nowadays. This paper presents the numerical modeling application to quantitative and qualitative analysis of storm-water sewer system in conditions of the selected urbanized area in the town of population reaching 40 000. The US EPA's (United States Environmental Protection Agency) software SWMM 5 was applied to our studies. Three different rainfall events of various time and intensity were applied to our research. The presented analysis was based on sewage flow velocity, wastewater table height in the pipelines and the load of pollutants leaving the sewerage system. The sewage flooding from several chambers was observed. Our studies reveals also the fact that the studied system is partially undersized and the observed concentration of TSS entering the receiver exceeds the maximum value allowable by the local standards. According to the lacking model calibration, our observations should be treated as the preliminary studies.

Keywords: storm sewer, numerical modeling, quantitative analysis, qualitative analysis

Operation of the municipal storm water systems, in accordance to variable rainfall events, possible increase and development of urbanized area, changes in sealing of drained surfaces and increased usage of road transportation vehicles may result in variable hydraulic conditions of sewage flow and pollutants concentrations and loads

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entering the sewage receiver. Additionally, periodical and temporal gathering of water in various types of manholes, in some cases resulting in flooding, may appear. Possibility of periodical flooding of drained areas should be certainly treated as costly disadvantageous phenomena, seriously affecting the everyday life of municipal settlement. Increase of concentrations and loads of pollutants transported by storm sewage may deteriorate the quality of water in the storm wastewater receiver [1–4].

Storm wastewaters, as it was frequently reported in literature, according to type and manner of drained urbanized area usage contain significant concentrations of pollutants *eg*: *total suspended solids* (TSS), *chemical oxygen demand* (COD), *biochemical oxygen demand* (BOD), *total nitrogen* (TN), *total phosphorus* (TP), heavy metals and oil derivatives [5–7]. As a result, according to European Water Frame Directive [8], in many European countries, the application of storm water drainage directly discharging untreated storm wastewaters into surface receivers, *ie*, usually rivers, is being limited in favour of solutions based on collection and treatment of storm sewage in location of their generation [9, 10]. Hence, the analysis of the influence of storm sewage discharge on receiver's water quality seems to be requisite.

Management of the complex storm water systems for different rainfall events and various possible manners of network development for basins of variable degree of sealing may be supported by numerical modeling. One of the most popular models applied in multivariate calculations is SWMM 5 (*Storm Water Management Model*) developed and supported by United States Environmental Protection Agency (US EPA). This model allows the dynamic quantitative and qualitative calculations of storm water network operation – the quality of offered calculations were repeatedly positively verified [4, 11, 12].

Presented studies focused on quantitative and qualitative analysis of storm water sewer system operation for the city of Swidnik, Poland. Our researches were based on numerical calculations performed by SWMM 5. Flow velocity of storm wastewater, storm water table height in links and nodes of the system, possible flooding as well as concentrations and loads of TSS, TN and TP at discharge location were selected as factors of our analyses.

Materials and methods

The considered urbanized catchment of area 2.47 km² covered the municipal system of storm water drainage the town of Swidnik, Poland. The total length of storm water system reached the value of approx. 48 km, the network is constructed of concrete pipes of diameters from DN 200 to DN 1600. Storm wastewaters are delivered directly to melioration drainage open ditch and then transported to the Stawek-Stoki river.

Numerical modeling of studied storm water network operation were performed by SWMM 5 [13]. The developed numerical model of existing network, based on documentation accessed by system operator, is consisting of 500 subcatchments, 473 nodes, 476 links and a sewage receiver. Geometrical characteristics of the existing system and hydraulic parameters of pipes were read from the map and assumed basing on the SWMM 5 documentation [14]. The described model was presented in Fig. 1.



Fig. 1. Scheme of modeled basin

Our numerical calculations were conducted for three different rainfall events (various time duration and intensity of rain). The characteristics of applied rainfall events were obtained from the local weather station in Felin, district of Lublin, Poland, approx. 3.0 km from the Swidnik city limits.

Unit runoff for rain No. I of duration $t = 15$ h was assumed as $2.67 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{ha}^{-1}$, rainfall event No. II $t = 15$ h $4.33 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{ha}^{-1}$, and event No. III $t = 4$ h $18.47 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{ha}^{-1}$. The precise information about rainfall events assumed to the numerical calculations are presented in Table 1 while its time-varied distribution is shown in Fig. 2.

Table 1

Characteristics of applied rainfall events

Rainfall characteristics	Rain No. I	Rain No. II	Rain No. III
Rainfall event time duration [h]	15	15	4
Total rainfall height [mm]	14.40	23.40	26.60
Mean rainfall intensity [$\text{mm} \cdot \text{h}^{-1}$]	0.96	1.56	6.65
Unit runoff [$\text{dm}^3 \cdot \text{s}^{-1} \cdot \text{ha}^{-1}$]	2.67	4.33	18.47

Qualitative numerical calculations were based on implemented in SWMM 5 equations of pollutants buildup and washoff on the basin surface. The exponential model of pollutant buildup and *event mean concentration* (EMC) model of pollutant washoff were selected [13, 14]. Input data were applied according to literature studies for three various types of land use (residential, undeveloped and transportation) distinguished in the studied catchment [5, 15, 16].

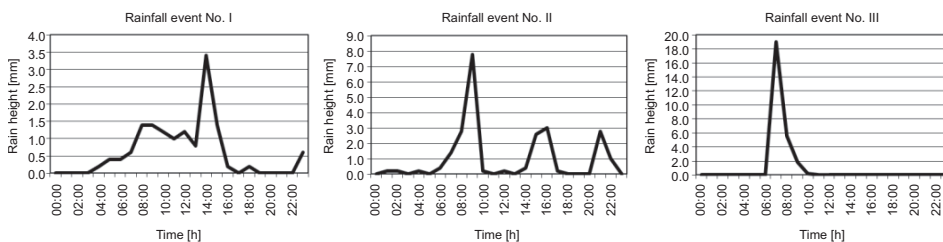


Fig. 2. Time-varied intensity of rainfall events applied to numerical calculations

Event mean concentration is a flow-weighted average value of selected pollutant concentration for a studied rainfall event. Definition of EMC may be described as follows [17]:

$$EMC = \frac{\sum C_i Q_i}{\sum Q_i}$$

where: C_i – concentration of studied pollutant,
 Q_i – storm water volumetric flow rate.

The input data set for TSS, TP and TN transport modeling was based on literature studies [5, 15, 18–22].

The presented numerical model of storm water network in Swidnik, Poland requires further empirical calibration based on multiple *in situ* measurements of qualitative and quantitative characteristics of studied system.

Table 2

Models and input data applied to TSS, TP and TN modeling

Type of data		Pollutant buildup		Pollutant washoff	
Model of pollutant		$B = C_1 (1 - e^{-C_2 t})$ B – pollutant buildup [mg · m ⁻²] C ₁ – maximum buildup possible [mg · m ⁻³] C ₂ – buildup rate constant [d ⁻¹] t – time [d]		$W = C_3 \cdot Q^{C_4}$ W – concentration of pollutant in surface runoff C ₃ – washoff coefficient, equal to EMC [-] C ₄ – exponent, C ₄ = 1 [-] Q – surface runoff flow rate [dm ³ · s ⁻¹]	
Applied values	Residential area	TSS	C ₁ = 50 [mg · m ⁻²] C ₂ = 0.3 [d ⁻¹]	TSS	EMC = 119.5 [-]
		TP	Co-pollutant to TSS 58 mg TP per kg TSS	TP	EMC = 0.47 [-]
		TN	Co-pollutant to TSS 550 mg TN per kg TSS	TN	EMC = 2.01 [-]
	Undeveloped area	TSS	C ₁ = 100 [mg · m ⁻²] C ₂ = 0.3 [d ⁻¹]	TSS	EMC = 206.5 [-]
		TP	Co-pollutant to TSS 60 mg TP per kg TSS	TP	EMC = 0.28 [-]
		TN	Co-pollutant to TSS 420 mg TN per kg TSS	TN	EMC = 2.46 [-]
	Transportation area	TSS	C ₁ = 70 [mg · m ⁻²] C ₂ = 0.3 [d ⁻¹]	TSS	EMC = 89.0 [-]
		TP	Co-pollutant to TSS 26 mg TP per kg TSS	TP	EMC = 0.39 [-]
		TN	Co-pollutant to TSS 430 mg TN per kg TSS	TN	EMC = 2.46 [-]

Results and discussion

The results of our calculations were presented in Figs. 3–9 and in Table 3. Our calculations showed that for all the cases studied, the velocity triggering self-purification of storm water pipelines is achieved in the significant number of pipes – from



Fig. 3. Nodal flooding and flow velocities observed for Rain No 1



Fig. 4. Nodal flooding and flow velocities observed for Rain No II



Fig. 5. Nodal flooding and flow velocities observed for Rain No III



Fig. 6. TSS concentration on subcatchments surface and in storm water pipelines for Rain No III



Fig. 7. TP concentration on subcatchments surface and in storm water pipelines



Fig. 8. TN concentration on subcatchments surface and in storm water pipelines

approx. 60 % for the rain No. I (Fig. 3) to the over 80 % for the most intensive rainfall No. III (Fig. 5).

Figure 3 shows the case of rainfall event of the lowest height and intensity for which the velocity of flow below $0.3 \text{ m} \cdot \text{s}^{-1}$ were noted in 14.1 % of pipelines and between $0.3\text{--}0.6 \text{ m} \cdot \text{s}^{-1}$ in 19.3 %. The modeled flow velocity above $0.6 \text{ m} \cdot \text{s}^{-1}$ was achieved in 66.6 % of pipelines.

The light improvement of hydraulic conditions of flow was observed in case of rainfall event No II. The velocity of flow below $0.3 \text{ m} \cdot \text{s}^{-1}$ was observed in 13 % pipelines and between $0.3\text{--}0.6 \text{ m} \cdot \text{s}^{-1}$ in 14.7 % of pipes.

The best conditions of flow were observed in case of the extreme rainfall event No. III. The velocity of flow below $0.3 \text{ m} \cdot \text{s}^{-1}$ was observed in 4 % pipelines and between $0.3\text{--}0.6 \text{ m} \cdot \text{s}^{-1}$ in 10.5 % of pipes. However, the extensive modeled flooding from 34 chambers was noted in case of rain No. III (see Fig. 3). Flooding for the others applied rainfall events was of lesser significance, it appeared only in one and three chambers for rain No. I and No. II, respectively.

Table 3

Results of quantitative and qualitative calculations for studied storm water network

Results	Unit	Rain No. I	Rain No. II	Rain No. III
Flow velocity [$\text{m} \cdot \text{s}^{-1}$] < 0.3	[%]	16.60	11.14	6.30
Flow velocity [$\text{m} \cdot \text{s}^{-1}$] > 0.6	[%]	59.66	77.31	78.99
Number of chambers endangered by flooding	[-]	1	3	34
TSS max concentration	[$\text{mg} \cdot \text{dm}^{-3}$]	142.16	149.98	128.18
TP max concentration	[$\text{mg} \cdot \text{dm}^{-3}$]	0.41	0.42	0.51
TN max concentration	[$\text{mg} \cdot \text{dm}^{-3}$]	2.37	2.42	2.94

Results of our qualitative calculations presented in Fig. 6, 7 and 8 showed that, the maximum observed TSS concentration, reaching the value close to $150 \text{ mg} \cdot \text{dm}^{-3}$ exceeds the values allowable by Polish standards ($100 \text{ mg} \cdot \text{dm}^{-3}$) [23]. The graphical presentation of time dependant changes of TSS, TP and TN loads is shown in Fig. 3. It's clearly visible, that time-varying loads of tested pollutants reflect, to some extent, the shape of rainfall events intensity curves. Changes in shape are caused by the time delay from the moment in which rain achieves drainages surfaces, enters storm water network and finally, reaches its outflow.

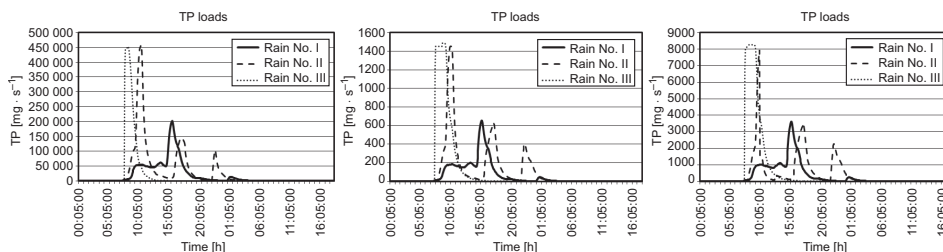


Fig. 9. Time-varying TSS, TP and TN loads at the outflow of modeled system

The exceeding of allowable concentration for calculated values of TSS along the main pipeline during the time of maximum network load for the rainfall event No III is clearly visible in Fig. 6.

The calculated TSS, TP and TN maximum concentrations for all applied rainfall events are in good agreement with values presented in literature reports [5, 17, 20, 21, 24], including EMC (Event Mean Concentration) values for various low and medium density urban catchments compiled by Park et al [12].

Summary

Our studies proved suitability of numerical modeling application to quantitative and qualitative analysis of storm water network development in conditions of Swidnik city, Poland. The obtained results show the satisfactory hydraulic conditions of storm wastewater flow in the clear majority of pipelines for every tested rainfall. But we observed also the insufficient capability of the modeled network in sewage disposal for the rain of the highest intensity. As the result, the intensive flooding significantly disturbing the life of urbanized community was observed. The excess of acceptable by actual local standards concentration of TSS along significant part of pipelines and in storm water discharged to the receiver was observed for the each studied variant of numerical calculations. The calculated concentrations and loads of TN and TP reflects the modeled changes of TSS concentration, according to the assumption of assigning TN and TP as the co-pollutants of TSS, which, reflects the fact of high absorptive surface of suspended soils accumulating various adsorbents. We consider further studies focused on assessment of retention tank application as location of introductory wastewater treatment, also by decrease of storm water flow rate, allowing to reduce the loads of pollutants entering the receiver. Additionally, we plan to perform the monitoring of exiting storm water system allowing the future model calibration. According to the lack of model calibration the presented researches should be treated as preliminary studies.

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ILOŚCIOWA I JAKOŚCIOWA ANALIZA NUMERYCZNA FUNKCJONOWANIA SIECI KANALIZACJI DESZCZOWEJ

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Abstrakt: Funkcjonowanie miejskich systemów kanalizacji deszczowej, na które wpływa wzrost powierzchni odwadnianej, zmienność opadów, zmiana stopnia uszczelnienia odwadnianych powierzchni oraz wzrost wykorzystywania transportu kołowego, związane jest z ciągłymi zmianami w przepływie ścieków, a także stężeniach i ładunkach zanieczyszczeń trafiających do odbiornika. Dlatego też standardem staje się wykorzystywanie modelowania numerycznego w wielowariantowej analizie warunków pracy oraz oddziaływania na środowisko kanalizacji deszczowej. W pracy przedstawiono próbę zastosowania modelowania numerycznego do ilościowej i jakościowej analizy warunków pracy kanalizacji deszczowej dla miejskiej jednostki osadniczej o liczbie mieszkańców wynoszącej 40 000 osób. Model sieci kanalizacji deszczowej rozpatrywanego miasta wykonano w programie SWMM5 opracowanym przez USEPA (United States Environmental Protection Agency). W badaniach modelowych wykorzystano trzy opady atmosferyczne charakteryzujące się różną intensywnością oraz czasem trwania opadu. Przedstawiona analiza została oparta na prędkościach przepływu ścieków, możliwości wypływu podpiętrzonych w studzienkach ścieków na powierzchnię terenu oraz ładunkach transportowanych zanieczyszczeń. Przeprowadzone badania wykazały możliwość wpływu ścieków ze studzienek połączonych lub rewizyjnych na powierzchnię odwadnianego terenu wynikające z częściowego niedowymiarowania badanego układu kanalizacyjnego. Odnotowano także przekroczenie aktualnych wartości dopuszczalnych stężenia zawiesiny ogólnej we wszystkich analizowanych wariantach obliczeń symulacyjnych. Ze względu na brak kalibracji modelu otrzymane wyniki należy traktować jako wyniki badań wstępnych.

Słowa kluczowe: kanalizacja deszczowa, modelowanie numeryczne, analiza ilościowa, analiza jakościowa

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COPPER AND ZINC CATIONS SORPTION BY WATER PLANTS – *Elodea canadensis* L. AND *Ceratophyllum demersum* L.

SORPCJA KATIONÓW MIEDZI I CYNKU PRZEZ ROŚLINY WODNE – *Elodea canadensis* L. I *Ceratophyllum demersum* L.

Abstract: Copper and zinc cations sorption kinetics by water plants *Elodea canadensis* L. and *Ceratophyllum demersum* L. was studied under laboratory conditions. The research was carried out under static conditions – at constant concentration and volume of the solution. The influence of the biomass preparation method on its sorption capacity was assessed. The model of pseudo-second-order reactions was applied in description of the heavy metals sorption kinetics. It was established that the dynamic equilibrium between the solution and biosorbent is achieved after approximately 50 minutes into the process, and that the applied preparation method of the plant biomass had a considerable influence on heavy metals sorption kinetics. The biomass *Elodea canadensis* L., dried and conditioned in demineralised water, showed the best sorption qualities. The carried out research results also show that *Elodea canadensis* L. and *Ceratophyllum demersum* L. are capable of sorbing a large part of heavy metal cations present in the solution, which allows for their use in water and effluent phytoremediation and in biomonitoring studies of aquatic ecosystems. In the experiment conditions, maximum 90 % cations of copper and 98 % of zinc were sorbed from the solution with *Elodea canadensis* L.

Keywords: water plants, heavy metals, sorption kinetics, model of pseudo-second-order reaction

Water plants (macrophytes) are a diverse group of organisms, which are difficult to define due to the links of the higher and lower water plants with the transient forms of land plants. One of the definitions assumes that macrophytes are the group of plants, which include vascular plants, water moss and algae generating macroscopic thallus. In Poland, the group of water plants includes all chara (*Charophyta*), some mosses (*Bryophyta*), a few ferns (*Pteridophyta*) and a small group of spermatophytes (*Spermatophyta*) [1–3].

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The research on the possibility of using certain species of water plants in phytoremediation processes of water and effluent polluted by heavy metals has been carried out for many years, as well as the biomonitoring research of water ecosystems. The studies assess their accumulation properties, resistance to high concentrations of pollution and the possibility of their repeated use in the processes of waters and sewage treatment. The research focuses mainly on the kinetics and equilibrium of the sorption process, interrelations between the concentration of pollution accumulated in plants and their environment as well as the influence of biotic and abiotic factors on these processes.

The pseudo-second-order reaction model is most frequently applied to describe the parameters of heavy metals sorption kinetics in biomass [4–6]. The studies of kinetics allow to define the constant reaction rate which, in turn, allows to assess sorption efficiency as a function of time. The Langmuir isotherm model is most frequently applied to describe the equilibrium parameters. The research authors emphasised good matching of this model to the obtained experiment data [4, 7].

The carried out research frequently focuses on defining the sorption capacity of specific types of macrophytes. The available data in literature show large differences in sorption characteristics between different species of water plants or within the same species. It may be caused by different research conditions or failure to consider all the factors, which influence the sorption processes [8, 9]. The most frequently studied species of water plants include: *Myriophyllum spicatum* L., *Lemna minor* L., *Elodea canadensis* L., *Ceratophyllum demersum* L. and the macrophytes of *Potamogeton* species [10–14]. The results of biomonitoring research, with the use of the above mentioned water plants species, show good correlation between concentrations of the pollution accumulated in plants and the environment, in which they live [15–17].

Two species of water plants present in Poland have been used in the research presented in this article. One of them is *Ceratophyllum demersum* L. (rigid hornwort). This is a common plant living in the Polish lowlands and uplands. It grows in stagnant and slowly flowing waters. It can be found both in large bodies of water and small ponds or water holes. It lives most often in degraded eutrophic reservoirs with alkaline reaction. Another macrophyte species used for the research is *Elodea canadensis* L. (Canadian waterweed). The plant originates from North America and it spread throughout most European continent, including Poland. It is a very expansive type of plant, present in various aquatic ecosystems: ponds, lakes, deeper ditches and slowly flowing rivers. It can be most frequently found in waters with medium fertility, which can be described as mesotrophic or sometimes eutrophic [18–20].

The objective of the carried out research was to assess the parameters of copper and zinc cations sorption kinetics by the prepared biomass *Elodea canadensis* L. and *Ceratophyllum demersum* L. The results can be used to determine a method for assessment of pollution of aquatic ecosystems by heavy metals and during planning of water and effluent remediation processes with the use of biomass.

Materials and methods

Water plants *Ceratophyllum demersum* L. obtained from a not much polluted water reservoir, previously a gravel and sand pit in the outskirts of Opole (PL), were used in the study. The plant *Elodea canadensis* L. was taken from the rivulet Czarnka, also flowing within the borders of Opole town. The water plants samples were cleaned from mechanical impurities and rinsed in demineralised water (conductivity $\kappa = 1.0 \mu\text{S}/\text{cm}$). The research was carried out with cleaned live plant samples and the biomass, which was dried at the temperature of 323 K. The dried biomass was stored in tightly sealed polyethylene containers.

The analysis and results interpretation method

The macrophyte samples with the mass of 0.5 g d.m. (d.m. – dry mass). were placed in a perforated container of approximately 15 cm³ volume and immersed in a 200 cm³ of copper sulfate or zinc sulfate solution. Prior to the experiment, the dried plant biomass was conditioned in demineralised water for 30 minutes. For comparison, the solutions from which sorption was carried out, were acidified to pH = 4, using hydrochloric acid. During the sorption process, the solutions were stirred vigorously with a magnetic mixer. In order to determine the short-term copper concentrations in the solution by the AAS method, samples of the solution (approximately 1.0 cm³) were taken during the process duration, straight from the container in which the sorption process was in progress. The sorption process was carried out for 50 minutes.

The kinetics was described with the use of the pseudo-second-order reaction model [21]:

$$\frac{t}{c_{M(s,t)}^*} = \frac{1}{k'' \cdot (c_{M(s,1)}^*)^2} + \frac{1}{c_{M(s,1)}^*} \cdot t \quad (1)$$

where: index M means concentration of the sorbed metal in the sorbent (s) after time (t) and in equilibrium (1), k'' – pseudo-second-order reaction constant rate. The value $c_{M(s,1)}^*$ should be treated as the maximum concentration of cations of the analysed metal, sorbed in water plants, being in equilibrium with the cations present in the solution.

Equipment and reagents

An atomic absorption spectrometer iCE 3500 (series 3000) made by Thermo Scientific, USA was used to determine heavy metals. The equipment was calibrated with the use of calibration standards from the company ANALYTIKA Ltd. (CZ). The value of the highest reference concentration of the copper and zinc solution used for the calibration, of 5 mg · dm⁻³ was assumed as the limit of linear dependence between the signal and the concentration.

The appliance made by Elmetron Sp.j. from Zabrze (PL): a pH meter CP551, which absolute reading error is $\Delta\text{pH} = 0.02$, was used to determine pH of the solutions in which water plants were immersed. MERCK reagents were used to prepare the solutions.

Quality control

Table 1 shows heavy metals concentrations, determined in the certified reference materials as BCR-414 *plankton* and BCR-482 *lichen*, prepared by the Institute for Reference Materials and Measurements, Belgium.

Table 1

Measured and certified values of heavy metals concentration in the BCR 414 *plankton* and BCR 482 *lichen* reference material

Metal	BCR 414 plankton					BCR 482 lichen				
	Certified value [mg/kg d.m.]	\pm Uncertainty	AAS		D^* [%]	Certified value [mg/kg d.m.]	\pm Uncertainty	AAS		D^* [%]
			Mean	$\pm SD$				Mean	$\pm SD$	
Cu	29.5	1.3	27.8	1.9	-5.8	7.03	0.19	6.54	0.18	-7.0
Zn	112	3	103	4	-8.0	100.6	2.2	93.9	2.5	-6.7

* Deviation: the relative difference between measured by AAS and certified concentrations in [%].

Results and discussion

The research carried out under static conditions, with constant solution volume and the sorbent mass, aimed at assessment of the sorption kinetics, depending on the method of plant biomass preparation.

Figures 1–4 show changes of the concentration of copper and zinc in *Ceratophyllum demersum* L. and *Elodea canadensis* L. [mmol/g d.m.], referred to the concentration of the analysed metal in the solution, from which the sorption was carried out [mmol/dm³]. The research was carried out with the use of differently prepared biomass. Initial concentration of metal $c_{M,0}$ was stated in the figures description.

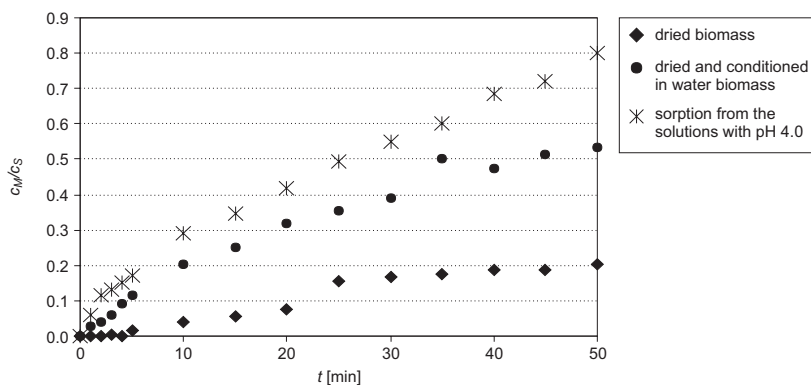


Fig. 1. Changes of copper concentrations in *Ceratophyllum demersum* L. (c_M) referred to copper concentration in the solution (c_S); $c_{Cu,0} = 0.016$ mmol/dm³

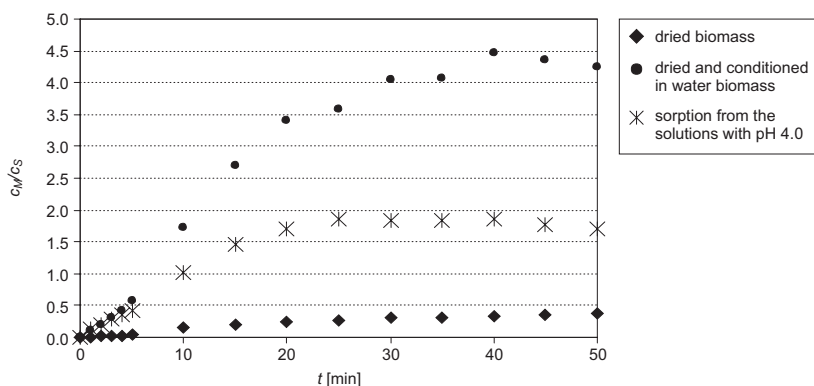


Fig. 2. Changes of copper concentrations in *Elodea canadensis* L. (c_M) referred to copper concentration in the solution (c_S); $c_{Cu,0} = 0.018 \text{ mmol/dm}^3$

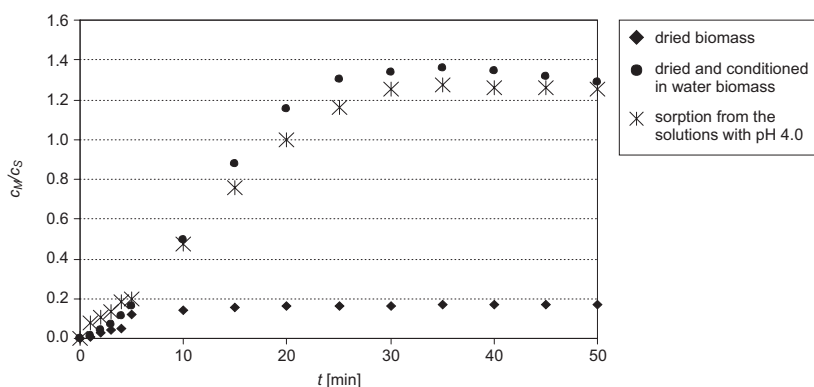


Fig. 3. Changes of zinc concentrations in *Ceratophyllum demersum* L. (c_M) referred to zinc concentration in the solution (c_S); $c_{Zn,0} = 0.018 \text{ mmol/dm}^3$

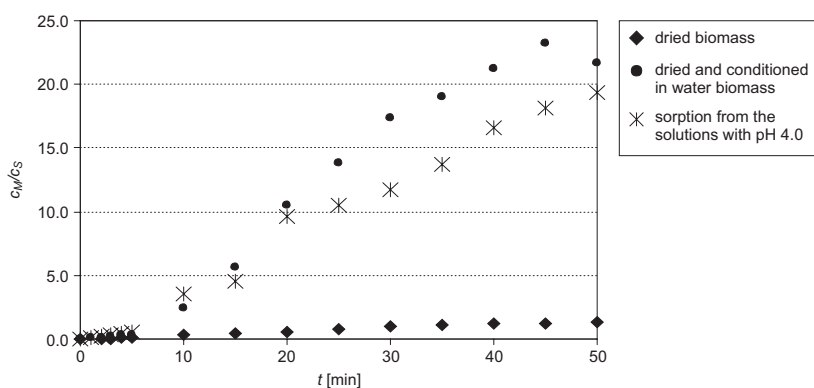


Fig. 4. Changes of zinc concentrations in *Elodea canadensis* L. (c_M) referred to zinc concentration in the solution (c_S); $c_{Zn,0} = 0.020 \text{ mmol/dm}^3$

When comparing the sorption parameters of the prepared plant biomass of the two analysed species, it should be stated that *Elodea canadensis* L. had much better sorption parameters. Of the two species, the biomass from *Elodea canadensis* L., dried and conditioned in demineralised water, showed the best capacity to accumulate Cu^{2+} .

Whereas in the case of *Ceratophyllum demersum* L., Cu^{2+} accumulated best in the biomass dried and conditioned in demineralised water, immersed in the solution with $\text{pH} = 4$. Special attention should be paid to the dried and conditioned in water biomass *Elodea canadensis* L., in which the ratio of the concentration of copper in the plant to its concentration in the solution is 5 times higher than in biomass *Ceratophyllum demersum* L., dried and conditioned in water, immersed in the solution with $\text{pH} = 4$. In the case of *Elodea canadensis* L., the equilibrium between the solution and biosorbent was achieved after approximately 20–30 minutes and, in the case of *Ceratophyllum demersum* L., the equilibrium was not achieved after 50 minutes. On the basis of the carried out research it can be stated that under the conditions, the initial concentration of

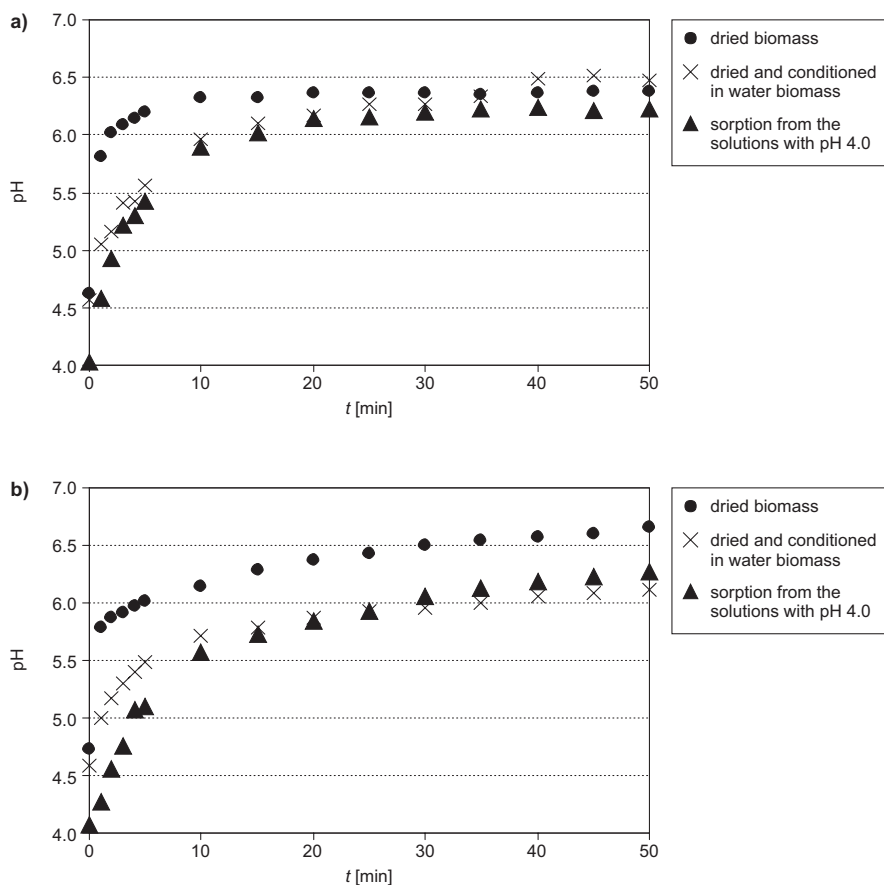


Fig. 5. Changes of the solutions pH during sorption of copper cations on the prepared biomass: a – *Elodea canadensis* L., and b – *Ceratophyllum demersum* L.

the copper solution (0.018 mmol/dm^3) during the sorption of 0.5 g of the dried and conditioned biomass *Ceratophyllum demersum* L. immersed in the solution with $\text{pH} = 4$, decreased by 64 %; whereas in the case of dried and conditioned in water biomass *Elodea canadensis* L., by 90 % ($c_0 = 0.018 \text{ mmol/dm}^3$).

In the case of zinc, the concentration of the sorbed metal versus the final concentration of the solution with *Elodea canadensis* L. was over 10 times higher than in the other plant (the biomasses were dried and conditioned in water). It can be stated that the initial concentration of the zinc solution (0.018 mmol/dm^3) during the sorption of 0.5 g of the dried and conditioned biomass *Ceratophyllum demersum* L., decreased under the conditions by 76 %; whereas in the case of dried and conditioned in water biomass *Elodea canadensis* L., by 98 % ($c_0 = 0.020 \text{ mmol/dm}^3$).

The graphs in Figs. 5 and 6 show pH changes of the solutions during the Zn^{2+} and Cu^{2+} sorption process by the prepared biomass *Elodea canadensis* L. and *Ceratophyllum demersum* L.

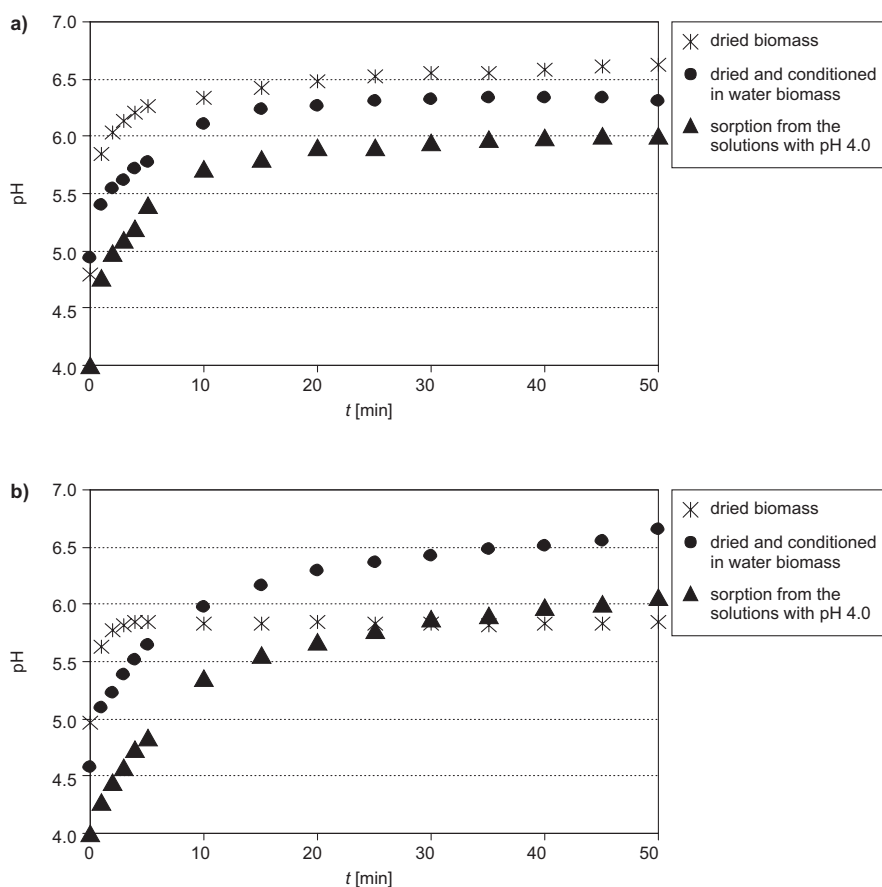


Fig. 6. Changes of the solutions pH during sorption of zinc cations on the prepared biomass: a – *Elodea canadensis* L., and b – *Ceratophyllum demersum* L.

It results from the graphs shown in Figs. 5 and 6, that the process of sorption of Cu^{2+} and Zn^{2+} ions on the prepared water plants biomass, is accompanied by the sorption of H^+ ions. During the sorption of the analysed heavy metals, pH of the solutions increased in all analysed cases to the level within the values of 6.0–7.0.

The graphs in Figs 7–10 show kinetics of the sorption of copper and zinc cations, described by a pseudo-second-order equation (relation 1).

The presented graphs do not show the first 10 minutes of the sorption process because the kinetics changes are not linear. A similar phenomenon can be noticed in the case of copper cations sorption by alga *Palmaria palmata*. This is probably the result of the parallel sorption of hydrogen cations, which is intense during the first 10 minutes of the process [22].

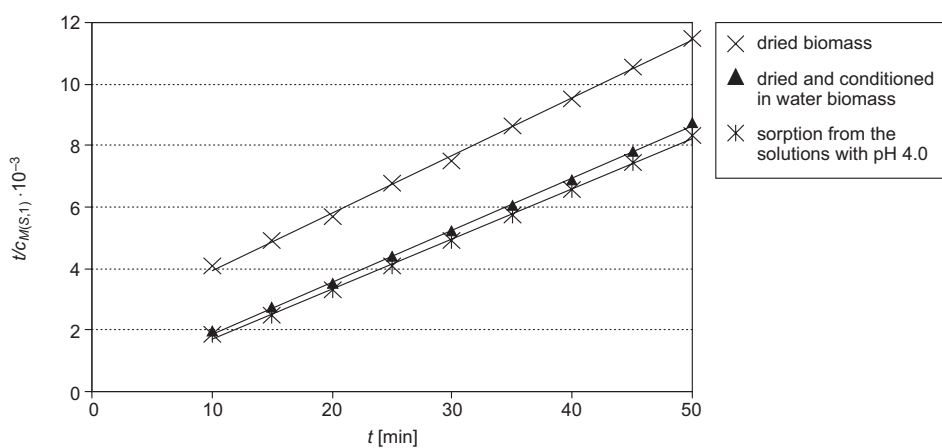


Fig. 7. Kinetics of the sorption of copper cations by *Elodea canadensis* L.

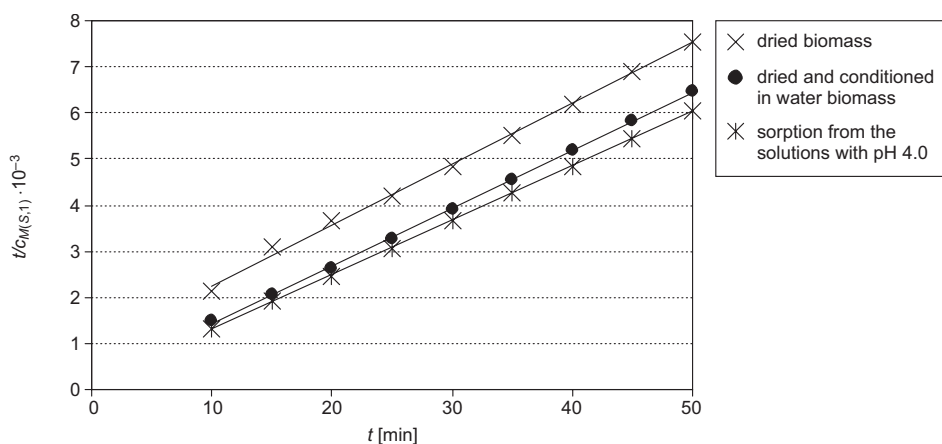


Fig. 8. Kinetics of the sorption of zinc cations by *Elodea canadensis* L.

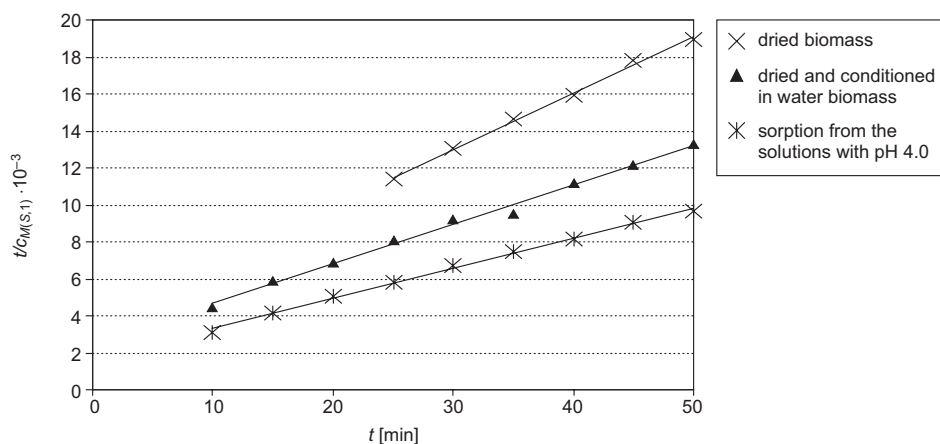


Fig. 9. Kinetics of the sorption of copper cations by *Ceratophyllum demersum* L.

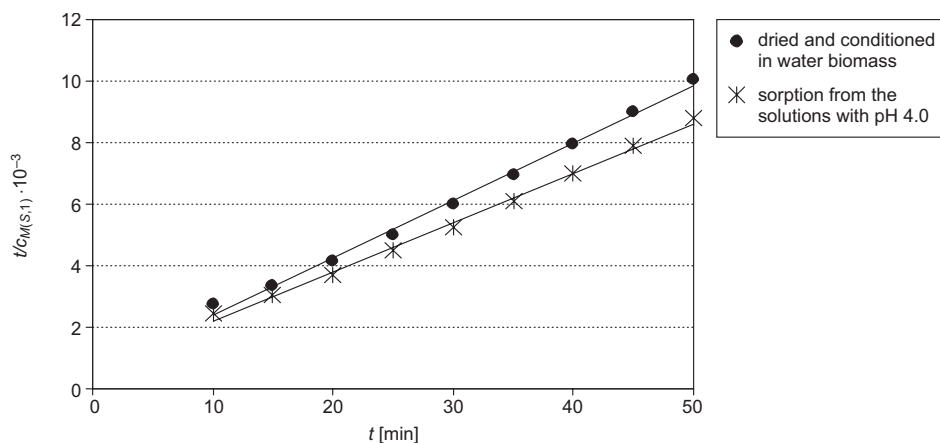


Fig. 10. Kinetics of the sorption of zinc cations by *Ceratophyllum demersum* L.

Table 2 shows a summary of statistical parameters of slopes of the straight lines presented in Figs. 7–10 and the calculated values of the constant reaction rate k'' [$\text{mmol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$].

The data included in the table show the appropriate application of the pseudo-second-order model to the description of copper and zinc sorption kinetics by *Elodea canadensis* L. and *Ceratophyllum demersum* L. The standard error of the slope of the straight line does not exceed 2 %. The standard error of the absolute term is much higher, within the range from 5 to 70 %. Constant rates of ion exchange described by the pseudo-second-order reaction model are within the range from 2 to 812 $\text{mmol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$. Due to the considerable uncertainty of the absolute term determination, these values are approximate.

Table 2

Statistical parameters of slopes of the straight lines $y = a \cdot x + b$ presented in Figs. 7–10 and the calculated values of the constant reaction rate

Preparation method	a	$\pm SD_a$	b	$\pm SD_b$	R^2	k''
COPPER						
<i>Elodea canadensis</i> L.						
Dried biomass	184.5	3.2	2167	103	0.997	424
Dried and conditioned in water biomass	169.1	1.5	177,0	48,0	0.999	2.70
Sorption from the solutions with pH = 4	161.1	2.0	139,0	66,0	0.998	2.00
<i>Ceratophyllum demersum</i> L.						
Dried biomass	305.1	8.8	3856	340	0.996	812
Dried and conditioned in water biomass	213.6	6.1	2254	198	0.994	509
Sorption from the 10 solutions with pH = 4	163.2	3.5	167,0	116	0.996	286
ZINC						
<i>Elodea canadensis</i> L.						
Dried biomass	157.3	4.3	1656	139	0.994	290
Dried and conditioned in water biomass	125.8	0.9	162,0	29,0	0.999	3.50
Sorption from the solutions with pH = 4	118.0	0.4	133,0	13,0	0.999	2.50
<i>Ceratophyllum demersum</i> L.						
Dried and conditioned in water biomass	185.7	5.0	567	164	0.994	29
Sorption from the solutions with pH = 4	160.0	3.8	620	124	0.996	40

SD – standard error, R^2 – coefficient of determination, k'' – constant reaction rate [$\text{mmol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$].

Summary and conclusions

The presented research results show that the dried and conditioned in water biomass *Elodea canadensis* L. had the best kinetic parameters. Thus, it was proved that the plant biomass preparation method considerably influences its sorption characteristics. Prior conditioning of plant samples in demineralised water considerably improves the capacity to accumulate copper and zinc. Thanks to good sorption properties, the studied plants can be used in future in phytoremediation of waters and effluent polluted with heavy metals and, thanks to the proportional sorption versus the concentration in a solution, in biomonitoring research of aquatic ecosystems.

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SORPCJA KATIONÓW MIEDZI I CYNKU PRZEZ ROŚLINY WODNE – *Elodea canadensis* L. I *Ceratophyllum demersum* L.

Samodzielna Katedra Biotechnologii i Biologii Molekularnej
Uniwersytet Opolski

Abstrakt: Zbadano w warunkach laboratoryjnych kinetykę sorpcji kationów miedzi i cynku przez rośliny wodne: *Elodea canadensis* L. i *Ceratophyllum demersum* L. Badania prowadzono w warunkach statycznych – przy stałym stężeniu i objętości roztworu. Dokonano oceny wpływu sposobu preparowania biomasy roślinnej na jej właściwości sorpcyjne. Do opisu kinetyki sorpcji metali ciężkich wykorzystano model reakcji

pseudo-drugowego rzędu. Stwierdzono, że stan równowagi dynamicznej pomiędzy roztworem a biosorbentem ustala się po około 50 minutach trwania procesu oraz, że sposób preparowania biomasy roślinnej istotnie wpływa na kinetykę sorpcji metali ciężkich. Najlepszymi właściwościami sorpcyjnymi charakteryzowała się suszona i kondycjonowana w wodzie zdeminielizowanej biomasa *Elodea canadensis* L. Wyniki przeprowadzonych badań wskazują również, że *Elodea canadensis* L. i *Ceratophyllum demersum* L. są w stanie zasorbować dużą część kationów metali ciężkich obecnych w roztworze, co pozwala na ich wykorzystanie w fitoremediacji wód i ścieków oraz w badaniach biomonitoringowych ekosystemów wodnych. W zadanych warunkach prowadzenia eksperymentu z roztworu, w którym umieszczono *Elodea canadensis* L. zasorbowano maksymalnie 90 % kationów miedzi i 98 % kationów cynku.

Słowa kluczowe: rośliny wodne, metale ciężkie, kinetyka sorpcji, model reakcji pseudo-drugowego rzędu

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CHROMIUM CONTENT IN SOILS AND PLANTS IN THE AREA UNDER INFLUENCE OF MMP “BOLESŁAW” ENTERPRISE IN BUKOWNO NEAR OLKUSZ

ZAWARTOŚĆ CHROMU W GLEBACH I ROŚLINACH W REJONIE ODDZIAŁYWANIA ZAKŁADÓW „BOLESŁAW” W BUKOWNIE KOŁO OLKUSZA

Abstract: Chromium belongs to the group of trace elements. Plants take it up from the substratum passively, therefore Cr content in plants is usually correlated with its concentrations in the soil solution. Toxic effect of chromium on plants depends both on its degree of oxidation and on the kind of compound in which it occurs. Due to the hazard of excessive chromium accumulation in plants in the areas with its elevated contents, particularly post-industrial and transformed areas, an on-going monitoring of this metal content in soils and fodder plants is recommended. The investigations were conducted to define and describe chromium transfer in the soil-plant system in the areas with various degrees of heavy metal pollution, using Surfer 8.0 programme for the presentation of spatial distribution of the metal in plants and soil in the area under investigations. The investigated area covered 100 km² in the vicinity of MMP (Mine and Metallurgical Plants) “Boleslaw” SA in Bukowno near Olkusz. Samples of soil and plant material were collected in 139 localities, during the period from June to August 2008. In each investigated point soil was sampled from two layers: 0–10 cm and 40–50 cm, together with the aboveground parts of mono- and dicotyledonous plants. In dissolved samples of plant and soil material chromium content was assessed using atomic absorption spectrometer with inductively coupled argon plasma (ICP-AES).

Soils from the investigated area revealed diversified contents of chromium, however no diversification was observed between the analysed soil layers. Slightly higher values occurred in the soils from 0–10 cm layer, particularly in the immediate vicinity of “Boleslaw” enterprise. Chromium accumulation in the mono- and dicotyledonous plants growing around MMP “Boleslaw” enterprise revealed weak diversification. No significant differences were observed either in the chromium accumulation in both analysed plant groups.

Keywords: chromium, mono- and dicotyledonous plants, MMP “Boleslaw” SA

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Introduction

Chromium belongs to trace element group. It is passively absorbed by plants from the substratum, so Cr content in the individual plant parts is the resultant of its concentration in the soil solution. Plants tolerate chromium in the amounts between 1 and 24 mg · kg⁻¹ d.m. Chromium toxicity for plants depends on both the degree of its oxidation and the kind of compounds in which it occurs [1].

The soil reaction [2], organic matter content and soil redox potential [3, 4] are the main factors affecting this element availability to plants and the form in which it occurs in the soil environment [1]. In the soil environment chromium occurs on two levels of oxidation Cr³⁺ – the form hardly absorbed by plants and Cr⁺⁶ – the easily absorbed form [5], but in excessive amounts both forms become toxic for plants and animals [2, 6, 7].

Excessive quantities of chromium in soil may occur in places of chromate containing waste storage, on wood calcination sites, in places of textile manufacturing, electric and thermal energy generating, as well as in the areas where sewage sludge are used for fertilization [8]. Besides, soils formed from metamorphic rocks may have naturally high concentrations of chromium of geochemical origin [1].

Due to the hazard of excessive chromium accumulation in plants and its considerable toxicity, an on-going monitoring this metal concentrations in soils and plant material meant for animal feed is recommended. It applies to areas with elevated heavy metal content in soils, particularly in post-industrial and anthropogenically transformed areas, such as among others the region in the vicinity of MMP (Mine and Metallurgical Plants) “Boleslaw” SA in Bukowno.

Presented investigations aimed at defining and describing chromium transport in the soil-plant system in the area under the influence of MMP “Boleslaw” SA in Bukowno near Olkusz, using Surfer 8.0 programme for spatial distribution of the analysed metal in the soil and plants.

Material and methods

The investigated area is situated in the southern part of Poland, on the border of the Malopolska and Silesia regions (Fig. 1). It covers the area of 100 km² surrounding MMP (Mine and Metallurgical Plants) “Boleslaw” SA in Bukowno near Olkusz.

The area of samples collection was divided into two zones: the first in the immediate vicinity of the enterprise, in which two sampling points were chosen at random for collecting 2 samples per 1 km² and the second situated at a longer distance from the enterprise, where 1 sample was collected per 1 km². The sampling method was so-called square net. Soil samples were collected in 139 points determined as above from the 0–10 cm and 40–50 cm soil layers. Moreover, the above-ground parts of mono- and dicotyledonous plants were sampled.

The following basic properties were determined in soils from both analysed layers:

- pH by potentiometric method in a suspension of 1 mol · dm⁻³ KCl solution,
- granulometric composition by Bouyoucose-Casagrande’s method in Proszynski’s modification,

- organic carbon content by Tiurin’s method,
- soil sorption capacity (hydrolytic acidity and base exchange capacity by Kappen’s method [10].



Fig. 1. Sampling sites in the region close to MMP “Boleslaw” SA [9]

Also total chromium concentrations were assessed in all collected soil samples. The samples were dissolved in a mixture of nitric and perchloric acids (2:1, v/v), after previous organic matter mineralization in a muffle furnace at 450 °C [10].

The next stage of research involved determining the content of analysed element in collected plant material samples. Dried and ground plant material was dry mineralized in a muffle furnace at 450 °C for 12 hours. Incinerated samples were dissolved in nitric acid (1:2) [4].

Each sample of both soil and plant material was analysed in two replications and to each analysed series a blind sample was attached. If the analysis results from two parallel replications differed from each other by more than 5 %, subsequent two analyses of the same sample were conducted. In the dissolved plant and soil samples chromium content was assessed using atomic emission spectrometer with inductively coupled argon plasma ICP-AES JY 238 ULTRACE (Jobin-Yvon).

Statistical analysis and presentation of the obtained results were conducted with the use of Microsoft Excel 2007 calculation sheet, Statistica 9.0 programme and SURFER 8.0 programme for data visualisation. It was used to create the maps of spatial distribution of chromium content in the analysed samples of soil and plant material.

Results and discussion

The soil samples presented in this paper, collected from the area of 100 km² around MMP “Boleslaw” SA in Bukowno near Olkusz, are characterized by a diversified cadmium, lead and zinc accumulations (from the concentrations close to assumed as natural to very high ones [11]).

Chromium contents in the vicinity of MMP “Boleslaw” SA assessed in both analysed soil layers: 0–10 cm and 40–50 cm were within a similar range 1.46–18.12 mg and 0.97–16.18 mgCr · kg⁻¹ d.m., respectively. However, diversification of the analysed element content in the lower soil layer was clearly higher and in both layers it was described by coefficients of variance 51.3 and 70.90 %, respectively (Table 1).

Table 1

Statistical parameters of total Cr content in soils and plants from the vicinity of MMP “Boleslaw” SA

Parameter	Cr content [mg · kg ⁻¹ d.m.]			
	Soil		Plants	
	0–10 cm	40–50 cm	Monocotyledonous	Ddicotyledonous
Minimum value	1.46	0.97	0.49	0.01
Maximum value	18.12	16.18	5.36	3.96
Arithmetic mean	7.18	4.83	1.57	1.32
Geometric mean	6.30	3.81	1.42	1.07
Median	6.23	3.52	1.35	1.07
Variation coefficient [%]	51.3	70.9	50.1	59.4

Numerical data sets describing polluted environment are usually characterised by skewed left data distribution [12, 13], therefore the characterization of chromium contents in the samples gathered in the vicinity of MMP “Boleslaw” SA used geometric mean, which is more approximate to median of a data set than arithmetic mean (Table 1). At a similar range of chromium occurrence in both investigated soil layers, geometric mean and median of its content in the top layer (6.30 and 6.23 mg · kg⁻¹ d.m., respectively) are much higher than in the samples collected from the 40–50 cm layer. If one assumes the above-mentioned statistical characteristics for the top soil layer as 100, then with the reference to the lower analysed soil layer they would be: 60 and 57, respectively (Table 1). It suggests that some quantity of chromium contained in the top soil layer might have originated from the atmosphere, from fallout of dust abundant in this metal. The hypothesis seems additionally supported by the spatial distribution of this element content in the soils of the investigated area (Fig. 2).

The highest Cr contents were assessed in the samples collected in the immediate vicinity of MMP “Boleslaw” SA and in the north-western part of the investigated area, *ie* in the direction of a nearby “Katowice” ironworks and other energy plants and industries of the Upper Silesia. On the other hand, analysing values of simple correlation coefficients between chromium accumulation in both layers of the studied

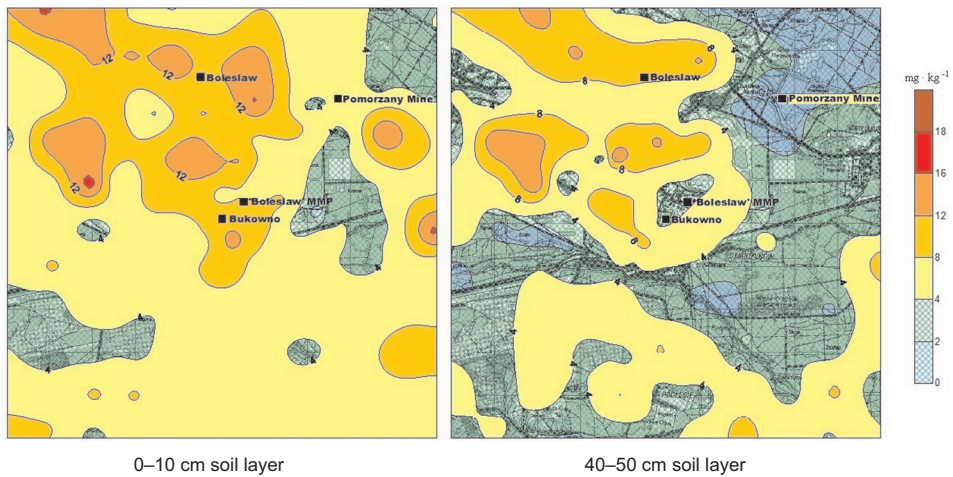


Fig. 2. Spatial distribution of chromium in soils from the vicinity of MMP “Boleslaw” SA

soils and their various physical and chemical properties, one should notice the strongest relationship between the content of analysed metal and occurrence of the finest soil fractions, described by correlation coefficients 0.72 and 0.78 in the upper and lower soil layer, respectively (Table 2). These values are substantial at the significance level $\alpha \leq 0.001$. On the other hand this relationship indicates that a big part of chromium in the studied soils may have its source in natural processes of bedrock transformations.

Table 2

Effect of soil properties on total Cr content in both analysed soil layers and in top parts of mono- and dicotyledonous plants – expressed as simple correlation coefficients (r)

Soil property	Soil layer [cm]	Cr _{tot} content		Cr _{tot} content	
		Soil layer [cm]		monocotyledonous	dicotyledonous
		0–10	40–50		
pH _{KCl}	0–10	0.22**	—	–0.003	–0.09
	40–50	—	0.25**	–0.03	0.03
Content of < 0.02 mm fractions	0–10	0.72***	—	–0.14	–0.33***
	40–50	—	0.78***	–0.09	–0.20**
Content of organic matter	0–10	0.52***	—	–0.12	–0.17*
	40–50	—	0.22**	–0.10	–0.08
Sorption capacity [T]	0–10	0.43***	—	–0.06	–0.18*
	40–50	—	0.39***	–0.11	–0.01
Cr _{tot} content	0–10	—	0.58***	–0.21**	–0.15
	40–50	0.58***	—	–0.04	–0.11

Simple correlation coefficient r significant at: * $\alpha \leq 0.05$, ** $\alpha \leq 0.01$ and *** $\alpha \leq 0.001$.

If the value of $20 \text{ mgCr} \cdot \text{kg}^{-1} \text{ d.m.}$ of soil suggested by Kabata-Pendias et al [14] is assumed as the highest permissible content of this metal in agricultural soils, all analysed soil samples meet this criterion. However, it should be noted, that many areas in the investigated terrain, a particularly in the immediate vicinity of MMP “Boleslaw” SA, should be excluded from cultivation because of excessive accumulation of heavy metals.

In order to determine bioavailability of chromium present in the studied soils, its concentrations were also assessed in mono- and dicotyledonous plants, which were growing in places where the soil was sampled.

Mean Cr contents in the analysed top parts of mono- and dicotyledonous plants were 1.42 and $1.07 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$, respectively (Table 1). The greatest content of the studied element, $5.36 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$ was assessed in a sample of monocotyledonous plants; it was about 1/3 bigger than the maximum content of this element determined in the dicotyledonous plant top parts. Assuming $20\text{--}30 \text{ mg} \cdot \text{kg}^{-1} \text{ d.m.}$ [13, 14] as the permissible chromium content in fodder, it should be stated this value has not been exceeded in any of the studied plant samples, so the analysed material may be used for fodder.

Spatial distribution of the analysed element in both plant groups was approximate, the highest Cr contents were registered in plants of both plant classes growing in points in various places of the investigated area (Fig. 3).

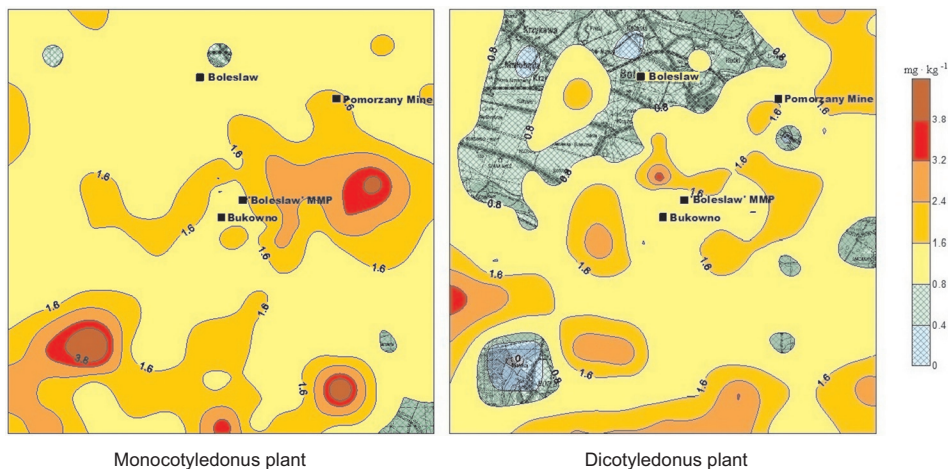


Fig. 3. Spatial distribution of chromium content in top parts of mono- and dicotyledonous plants in the vicinity of MMP “Boleslaw” SA

The places do not overlap the zones where the highest total chromium content in the studied soils was registered. It means that the assessment of total chromium content in soil cannot be an indicator for estimating its concentrations in plants growing in this soil. Considering the monocotyledonous plants, even a significant negative correlation ($r = -0.21$, $\alpha \leq 0.01$) was registered between this element concentrations in plants and soil (Table 2).

No apparent effect of the analysed properties of the studied soils on chromium accumulation in plants was registered (Table 2). A slightly lower uptake of this metal by plants growing in more compact soil, more abundant in organic matter was observed for the dicotyledonous class. If, following Kabata-Pendias et al [14], one assumes that chromium is passively absorbed from the soil solution by plants, its solubility in soil must be affected other soil properties not investigated in the presented research or it is a simultaneous resultant effect of several soil properties.

Conclusions

1. The analysed soils in the area of influence of MMP "Boleslaw" SA engaged in extraction and processing of lead-zinc ores, are characterized by a diversified chromium content which does not exclude agronomic use of these soils. Increased chromium concentrations were assessed in the soil around MMP "Boleslaw" SA and north-west of the enterprise.

2. Solubility and bioavailability of chromium in soil to a greater extent depends on various soil properties than on its total content in the substratum.

3. Chromium accumulation in monocotyledonous plants growing in the areas to various extent polluted with cadmium, lead or zinc was slightly higher than in dicotyledonous plants and in all cases did not lower the fodder value of these plants.

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ZAWARTOŚĆ CHROMU W GLEBACH I ROŚLINACH W REJONIE ODDZIAŁYWANIA ZAKŁADÓW „BOLESŁAW” W BUKOWNIE KOŁO OLKUSZA

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Abstrakt: Chrom należy do grupy pierwiastków śladowych. Jest on pobierany z podłoża przez rośliny biernie, przez co jego zawartość w roślinach jest zwykle skorelowana z zawartością chromu w roztworze glebowym. Toksyczne działanie chromu na rośliny zależy zarówno od jego stopnia utlenienia, jak również od rodzaju związku w jakim występuje. Ze względu na zagrożenie nadmierną kumulacją chromu w roślinach w terenach z podwyższoną zawartością chromu, szczególnie przemysłowych i przekształconych, zaleca się stały monitoring zawartości tego metalu w glebach i roślinach przeznaczonym na paszę. Celem przeprowadzonych badań było zdefiniowanie i opisanie transferu chromu w układzie gleba-roślina w terenach w różnym stopniu zanieczyszczonych metalami ciężkimi, z wykorzystaniem programu Surfer 8.0 do prezentacji przestrzennego rozmieszczenia metalu w roślinach i glebie na terenie objętym badaniami. Obszar badań obejmował 100 km² w sąsiedztwie Zakładów Górniczo-Hutniczych „Bolesław” SA w Bukownie koło Olkusza. Próbkę gleby i materiału roślinnego zebrano w 139 miejscach, w okresie od czerwca do sierpnia 2008 r. W każdym punkcie badań pobrano glebę z dwóch poziomów: 0–10 i 40–50 cm oraz części nadziemne roślin jedno- i dwuliściennych. W roztworzonych próbkach materiału roślinnego i glebowego oznaczono zawartość chromu przy użyciu spektrometru emisji atomowej z indukcyjnie wzbudzoną plazmą argonową (ICP-AES).

Gleby z badanego obszaru wykazywały zróżnicowane zawartości chromu, jednak nie stwierdzono znacznego zróżnicowania jego zawartości pomiędzy badanymi warstwami gleb. Nieco większe zawartości występowały w glebach z warstwy 0–10 cm, zwłaszcza w bezpośrednim sąsiedztwie ZGH „Bolesław” SA. Zawartość chromu w częściach nadziemnych roślin jedno- i dwuliściennych rosnących wokół ZGH „Bolesław” SA wykazywała słabe zróżnicowanie. Nie stwierdzono także znaczących różnic w nagromadzeniu chromu w obu badanych grupach roślin.

Słowa kluczowe: chrom, rośliny jedno- i dwuliścienne, ZGH „Bolesław” SA

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CONTENT AND FRACTIONAL COMPOSITION OF NICKEL IN ARABLE SOILS DEPENDING ON PHYSICOCHEMICAL PROPERTIES

ZAWARTOŚĆ I SKŁAD FRAKCYJNY NIKLU W GLEBACH UPRAWNYCH ZALEŻNIE OD ICH WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH

Abstract: The aim of this study was estimation of pseudo-total nickel content and its fractional composition in arable soils depending on their physicochemical properties. The research material consisted of samples taken from arable soil in 81 points of Podlasie Province. The content of pseudo-total nickel in soils and its fractional composition was determined with BCR method. The correlations between pseudo-total content of nickel, as well as its individual fractions and physicochemical properties of soils were evaluated.

It was found, that pseudo-total content of nickel was typical for uncontaminated soils and ranged from 2.0 to 14.4 mg · kg⁻¹. The share of acid soluble and exchangeable fraction was above 20 %, as compared to pseudo-total content. Reducible fraction comprised 20–40 %. The most of nickel was bound to organic matter. The factors which influenced fractional composition of nickel were determined. For the light soils it was content of soil fraction < 0.02 mm, granulometric composition and pH, while for medium-heavy soils, organic carbon and magnesium content, granulometric composition and content of soil fraction < 0.02 mm. The factors related to the changes of Ni content in light soils in fraction II and IV and for medium-heavy soils in fraction I, were not determined.

Keywords: nickel, soil, BCR method, metal fraction

Introduction

The natural content of elements, including trace elements, in arable soils is dependent on lithogenesis and pedogenesis [1]. The other sources of trace elements, such as mineral and organic fertilization, plant pesticides, irrigation, as well as wet and dry precipitation, are related to anthropogenic activity [2, 3]. It is well known, that they

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occur in soil in different forms, which are more or less mobile, that means bioavailable. Trace elements of anthropogenic origin are, in general, more mobile, than these of natural origin [4]. Mobility of metals is influenced mainly by physicochemical properties of soil, pH, content of organic matter, granulometric composition and management practices [5].

There are many methods for estimation of metal forms and their changes in soil, sequential extraction for example [6, 7]. There are a lot of schemes of this method [8]. For unification purposes the BCR method [9, 10] with its modifications [11] is increasingly used.

Nickel is essential for proper plant growth and development (it forms the active metallocenter of the enzyme urease) [12]. Excessive Ni amounts inhibit a large number of plant enzymes, cause disturbance of cation-anion and water balance in plant as well as inhibit development of lateral roots. Its total content in non-contaminated soils is up to $35 \text{ mgNi} \cdot \text{kg}^{-1}$ (in sandy soils about $15 \text{ mgNi} \cdot \text{kg}^{-1}$ and in heavy textured soils about $30 \text{ mgNi} \cdot \text{kg}^{-1}$) [13]. The total content of nickel is not adequate to estimate its behavior in soils. It's necessary to identify quantitative changes of its chemical forms.

The aim of this study was estimation of pseudo-total nickel content and its fractional composition in arable soils using BCR method, depending on their physicochemical properties.

Materials and methods

The research material consisted of samples taken from arable soil in 81 points of Podlasie Province. One point was selected in the majority of its districts. Each point was located on mineral soil used as arable land, without external source of contamination, like roads or industrial plants. The samples were collected from arable layer (0–30 cm) after plant harvest. Maize was cultivated in 14 points, cereals in 53 points, rape in 2 points, buckwheat in 2 points and the rest was taken from under grass on field cultivation. Basic physicochemical properties of soil samples there were determined: granulometric composition by Cassagrande's method with Proszynski's modification, organic carbon content by Tiurin's and pH in $1 \text{ mol} \cdot \text{dm}^{-3}$ KCl solution by potentiometric method. Available phosphorus and potassium by Egner-Riehm method, as well as magnesium by Schachtschabel method in soils were also determined. Based on the content of soil fraction $< 0.02 \text{ mm}$, soils were divided into two groups: very light and light and medium-heavy soils. Heavy soil was not taken into account, because this type does not occur in Podlasie Province. The pseudo-total nickel content was determined, after previous digestion in *aqua regia*, by means of FAAS technique using Varian AA-100 apparatus.

Modified BCR method with usage of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of Ni in soil samples. Extraction included four stages (fractions):

1. Acid soluble and exchangeable fraction (fraction I) – 1 g of soil in 100 cm^3 centrifuge tube with 40 cm^3 of $0.11 \text{ mol} \cdot \text{dm}^{-3}$ acetic acid was sonicated for 7 minutes (power – 20 W) at temperature $22 \pm 5 \text{ }^\circ\text{C}$. Then, the mixture was centrifuged for 20

minutes at 3000 g. Extract was separated for analysis. Residue with 20 cm³ of deionized water was sonicated for 5 minutes (power – 20 W) and centrifuged for 20 minutes at 3000 g. Water was discarded.

2. Reducible fraction, bound to Fe/Mn oxides (fraction II) – to the residue from the first step was added 40 cm³ of 0.5 mol · dm⁻³ hydroxylamine hydrochloride fresh solution, pH = 1.5, and sonicated for 7 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 minutes at 3000 g. Extract was separated for analysis. The residue was rinsed with deionized water, like in the first step.

3. Oxidizable fraction, bound to organic matter (fraction III) – to the residue from the second step was added 20 cm³ of 30 % hydrogen peroxide and sonicated for 2 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the volume of H₂O₂ was reduced to approx. 1 cm³ using water bath. To the moist residue was added 50 cm³ of 1 mol · dm⁻³ ammonium acetate and sonicated for 6 minutes (power – 20 W) at temperature 22 ± 5 °C. Then, the mixture was centrifuged for 20 minutes at 3000 g. Extract was separated for analysis. The residue was rinsed with deionized water, like in the previous steps.

4. Residual fraction (fraction IV) – the residue from the third step was extracted using concentrated HNO₃ with addition of 30 % H₂O₂. Extract was separated for analysis.

The content of studied element in fractions was determined by means of GFAAS technique using Varian AA-100 apparatus. The share of individual fractions in pseudo-total content of nickel was calculated.

Pearson correlation coefficients between all sets of data were calculated. It was assumed that they are significant above 0.65 or below –0.65. Since the correlation coefficients were non-significant, canonical factor analysis was made. Based on this analysis, for both groups of soil, factors which influenced fractional composition of nickel were determined.

Results and discussion

The content of soil fraction < 0.02 mm in very light and light soils ranged from 4 to 19 % (12 % on average) and in medium-heavy soils from 21 to 28 % (22 % on average) (Table 1).

The pH of the first group of studied soils was very differentiated and varied from 4.0 to 7.6. Among 35 soil samples, twelve were very acidic (pH < 4.5), eight were acidic (pH = 4.6–5.5), nine was slightly acidic (pH = 5.6–6.5) and the rest soils were neutral (pH = 6.6–7.2). The most of medium-heavy soils was characterized by higher pH values: only three samples came from very acidic soils, eleven samples were acidic and the rest were light acidic and neutral. Investigated soils were typical for Podlasie Province, that is light and acidic.

The content of organic carbon in both groups of soil was differentiated. In very light and light soils ranged from 8 to 37 g · kg⁻¹ (18 g · kg⁻¹ on average), and in medium-heavy soils from 7 to 42 g · kg⁻¹ (24 g · kg⁻¹ on average). The most of soils contained average amounts of phosphorus and magnesium, as well as low amount of potassium.

Table 1

Physicochemical properties of soils

Studied soils		Share of soil fraction < 0.02 mm [%]	pH	C _{org} [g · kg ⁻¹]	P ₂ O ₅	K ₂ O	Mg	Pseudo-total content of Ni
Very light and light soils n = 35	range	4–19	4.0–7.6	8–37	43–440	25–290	7–150	2.0–9.1
	\bar{x}	12	5.3	18	155	107	47	5.5
	median	13	5.2	15	121	9.5	38	5.25
Medium-heavy soils n = 46	range	21–28	4.1–7.8	7–42	22–420	32–484	17–226	2.6–14.4
	\bar{x}	22	6.1	24	137	132	97	7.8
	median	22	6.1	21	115	106	93	7.5

The pseudo-total content of nickel in very light and light soils ranged from 2.0 to 9.1 mg · kg⁻¹ and in medium-heavy soils from 2.6 to 14.4 mg · kg⁻¹. It means that studied soils contained natural amount of nickel, which is mainly influenced by parent rock.

Many authors report high differentiation of pseudo-total content of nickel in soils. According to Terelak et al [14] the content of nickel in soil ranged from 0.10 to 173 mg · kg⁻¹, in contrast, Gworek and Misiak [13] report that content ranged from 0.2 to 35.0 mgNi · kg⁻¹. The higher amounts of nickel can be found in soils derived from igneous and sedimentary rocks and the lower ones in soils derived from loams and sandy deposits [15]. The total content of metals indicates only degree of possible threat of soil, but not the binding forms of each element. That's why the sequential analysis is made, which shows the type of chemical binding forms of an element and potential threats related to its high bioavailability.

The percentage of nickel in fraction I of very light and light soils (Fig. 1) was increasing simultaneously with pH value and ranged from 17 to 25 %, as compared to

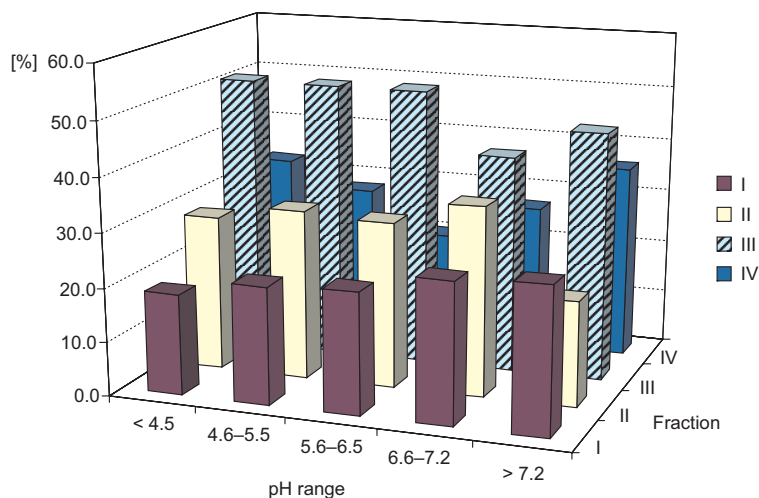


Fig. 1. Percentage of nickel fractions in pseudo-total its content in light and very light soils, depending on pH

pseudo-total content. Sloot et al [16] stated that the increase of nickel content in soil solution of soils with high pH values might be connected with the rise of solubility of organic matter. Due to this process the nickel can be released, what causes its content increase in soluble and exchangeable fraction in soils with neutral and alkaline reaction. In medium-heavy soils opposite trend was observed (Fig. 2).

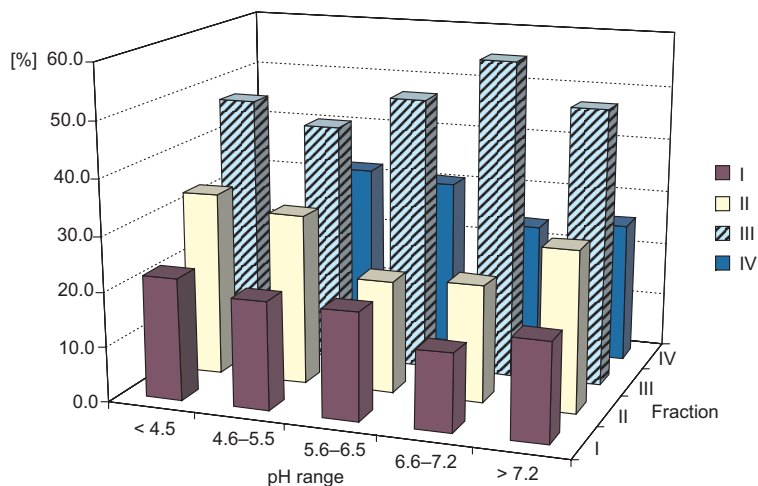


Fig. 2. Percentage of nickel fractions in pseudo-total its content in medium soils, depending on pH

In the most of light soils with very acidic, acidic and slightly acidic reaction the percentage of nickel bound to Fe/Mn oxides and hydroxides was increasing with pH value and decreased in soils with pH > 7.2.

In medium-heavy soils with pH \leq 7.2 the percentage of Ni in fraction II was decreasing with increase of pH value. In soils with pH > 7.2 the rise of percentage of Ni in fraction I and II was noted. Rooney et al [17] are reporting that sorption of nickel by Fe/Mn hydroxides is increasing simultaneously with decrease of soil acidity, what is proved by obtained results.

The organic matter applied to soil in large amounts causes the decrease of content of available for plants forms of metals, such as nickel [18]. The organic fertilizers are applied to soil in Podlasie Province even each year, due to the well developed cattle farming. It may contribute to decrease of mobility of trace elements, mainly in medium-heavy soils, what can be seen in the results of our studies.

The most of nickel was bound to organic matter (Figs. 1 and 2). The percentage of nickel in fraction III was influenced in small degree by soil reaction. It was similar in very light and light soils with very acidic, acidic and light acidic reaction. Among soils from this group with higher pH values the decrease of share of Ni about 10 % in discussed fraction was noted. The opposite trend was observed in medium-heavy soils (Fig. 2). The share of nickel in residual fraction of both groups of soils was mainly lower than 30 % of pseudo-total content.

Investigating distribution of nickel in individual fractions in dependence on content of organic carbon in soil, can be stated, that more of nickel in exchangeable fraction was in light soils (Fig. 3).

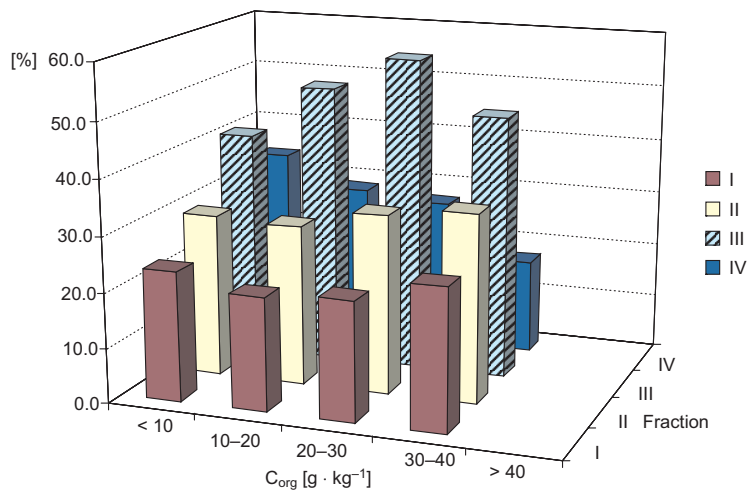


Fig. 3. Percentage of nickel fractions in pseudo-total its content in light and very light soils, depending on organic carbon content

The percentage of nickel in this case was about 20 % and was similar in all the investigated soils. In medium-heavy soils it was lower than 20 % (Fig. 4) and differentiated by content of organic carbon.

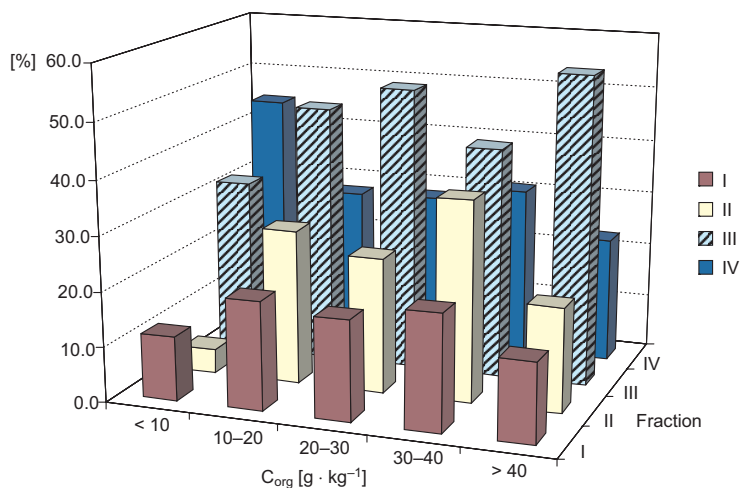


Fig. 4. Percentage of nickel fractions in pseudo-total its content in medium-heavy soils, depending on organic carbon content

The share of Ni in fraction II in very light and light soils was about 30 %, increasing with rise of organic carbon content. In medium-heavy soils such tendency was not observed and percentage of nickel in this fraction was lower. The most of nickel was in fraction III, bound to organic matter. The percentage in this case was increasing at the same time as the content of organic carbon in both groups of soil was rising and reached the most 50 %. The percentage of nickel in residual fraction, in both groups of soil, was the highest in soils which contained below $10 \text{ gC}_{\text{org}} \cdot \text{kg}^{-1}$ of soil and was decreasing simultaneously with increase of carbon content.

Many authors [17, 19, 20] emphasize, that availability and mobility of nickel in soil is dependent on lot of factors, including content of organic matter and iron compounds, as well as reaction. Canonical factor analysis, for both groups of soil, explains the above mentioned statement (Tables 2 and 3). In very light and light soils determined two factors which influenced the percentage of nickel in fraction I and III.

Table 2

Factor analysis of nickel fraction contents in light and very light soils

Factor	Content of Ni			
	Fraction I	Fraction II	Fraction III	Fraction IV
pH	0.02	-0.11	-0.69	0.10
C _{org}	0.45	-0.32	-0.01	0.40
P ₂ O ₅	-0.10	-0.09	-0.46	0.47
K ₂ O	-0.13	-0.03	-0.09	-0.09
Mg	0.21	0.47	-0.28	0.32
Content of soil fraction < 0.02 mm	0.88	0.06	-0.57	-0.12
Granulometric composition	-0.82	-0.01	-0.51	-0.53

Table 3

Factor analysis of nickel fraction contents in medium-heavy soils

Factor	Content of Ni			
	Fraction I	Fraction II	Fraction III	Fraction IV
pH	-0.51	-0.25	0.08	0.53
C _{org}	-0.53	-0.72	-0.21	0.24
P ₂ O ₅	0.12	0.17	0.52	0.04
K ₂ O	-0.02	0.00	0.02	0.12
Mg	-0.24	-0.16	-0.10	0.80
Content of soil fraction < 0.02 mm	-0.62	-0.25	-0.91	0.45
Granulometric composition	0.56	0.08	-0.91	0.58

The factors which explain the content of nickel in fraction I consisted of content of soil fraction < 0.02 mm and granulometric composition. The factor which affected the

Ni content in fraction III was pH of soil. The factors conditioning the changes of Ni content in fraction II and IV were not determined.

In studied medium-heavy soils were determined three factors which influenced the percentage of nickel in fraction II, III and IV. The content of organic carbon was the factor conditioning the changes of percentage of Ni in fraction II. The factors which explain the content of nickel in fraction III consisted of the content of soil fraction < 0.02 mm and granulometric composition. The factor which affects the Ni content in fraction IV was the content of magnesium. The factors which influenced the changes of nickel content in fraction I were not determined.

Conclusions

1. The studied soils were characterized by natural content of pseudo-total nickel.
2. The percentage of nickel in studied soils was the highest in fraction bound to organic matter and similar in other fractions.
3. The percentage of nickel in fraction I, in very light and light soils, was affected by content of soil fraction < 0.02 mm and granulometric composition, while in fraction III by pH. The percentage of nickel in fractions II, III and IV in medium-heavy soils was determined by organic carbon, granulometric composition and content of soil fraction < 0.02 mm, as well as magnesium content.

Acknowledgements

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ZAWARTOŚĆ I SKŁAD FRAKCYJNY NIKLU W GLEBACH UPRAWNYCH ZALEŻNIE OD ICH WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH

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Abstrakt: Celem niniejszej pracy było określenie całkowitej zawartości niklu i jego frakcji w glebach uprawnych Podlasia oraz określenie zależności między zawartością niklu i jego frakcji a właściwościami fizykochemicznymi gleb. Materiał badawczy stanowiły próbki pobrane z gleb uprawnych w 81 punktach województwa podlaskiego. Oznaczono zblizoną do ogólnej zawartość niklu i jego frakcji metodą BCR. Obliczono zależności korelacyjne między zawartością ogólną niklu i jego poszczególnych frakcji, a właściwościami fizykochemicznymi gleb.

Stwierdzono, że zawartość niklu ogółem była typowa dla gleb uprawnych niezanieczyszczonych i wahała się w szerokich granicach od 2,0 do 14,4 mg · kg⁻¹. Udział frakcji wymiennej w ogólnej zawartości niklu w badanych glebach wynosił ponad 20 %. Frakcja redukowalna stanowiła 20–40 % zawartości ogólnej. Najwięcej niklu było związane z substancją organiczną. Wyodrębniono czynniki wpływające na udział niklu w poszczególnych frakcjach. Dla gleb lekkich był to skład granulometryczny, zawartość frakcji spławialnej i pH, a w przypadku gleb średnich zawartość węgla organicznego, skład granulometryczny, zawartość frakcji spławialnej i zawartość magnezu. Nie wyznaczono czynników warunkujących zawartość niklu w II i IV frakcji gleb lekkich, a w przypadku gleb średnich zawartość tego metalu we frakcji I.

Słowa kluczowe: nikiel, gleba, metoda BCR, frakcje metali

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Lesław TEPER¹ and Tomasz KRZYKAWSKI³

HEAVY METALS SOIL CONTAMINATION INDUCED BY HISTORICAL ZINC SMELTING IN JAWORZNO

ZANIECZYSZCZENIE GLEBY METALAMI CIĘŻKIMI ZWIĄZANE Z HISTORYCZNYM HUTNICTWEM CYNKU W JAWORZNI

Abstract: The initial study of heavy metals (Cr, Cu, Ni and Mn) contamination was carried out on the 22 samples taken from 4 forest soil (podzol) profiles and 5 waste samples taken from 3 points of the historical zinc smelting area in Jaworzno, Southern Poland. XRD and pH analyses on the soil samples were done. The trace element concentrations were measured with the inductively coupled plasma optical emission spectrometry (ICP-OES) after mineralisation in concentrated HNO₃ (65 % Suprapur) and HCl (30 % Suprapur). Examined materials were ultra acidic to neutral, mostly very strong acidic. Total accumulations of trace elements in the soil varied from 21.91 to 119.32 mgCr, from 1.4 to 51.16 mgCu, from 2.15 to 36.16 mgNi and from 16.33 to 869.19 mgMn · kg⁻¹. In waste samples quantities of the same elements equalled 45.55–67.38 mgCr, 19.5–244.74 mgCu, 4.96–22.15 mgNi and 30.75–369.11 mgMn · kg⁻¹. Vertical distributions of examined metals were determined in each of soil profiles. The research revealed heavy metal pollution of studied soil. Influence of the historical smelter on the pollution is inferred, which changed soil environment to dangerous for humans, especially due to close proximity of abandoned industry to built-up and recreation areas as well as community gardens.

Keywords: zinc smelting, heavy metals, soil contamination

Introduction

Chromium, copper, nickel and manganese are natural and common components of the Earth's crust. The four elements account for 83 mgCr · kg⁻¹, 25 mgCu · kg⁻¹,

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44 mgNi · kg⁻¹ and 600 Mn · kg⁻¹ of upper continental crust mass [1]. Natural and anthropogenic sources contribute to the presence of these elements in environmental compartments, such as air, water, soil and plant. The mentioned elements are known as microelements and they are essential in metabolic processes for plants and animals [2]. However, they may also appear toxic for living organisms if their concentrations in soil environment increase over maximum tolerable values [3–6].

From among number of factors controlling availability of trace elements in the soil environment [7, 8], these of the crucial importance are the pH value and oxidation-reduction potential.

Anthropogenic activities, such as ore mining and smelting, power industry, waste dumping sites, and transport, are thought to be sources of the heavy metals – Cr, Cu, Ni and Mn – pollution in the industrially changed environment [9–12]. The areas characterised by strong development of the present-day or historical mining and metallurgy production, constitute a hazard of the heavy metal contamination in many countries [13–16], also in the Jaworzno town vicinity [17–19]. The transfer of toxic elements from industrial wastes, soils, water and air to plants is of great concern *eg* [20], particularly in the surrounding of community gardens or agricultural area.

The aim of this study is to find out if an abandoned long time ago zinc smelting factory and its partly reclaimed waste heap left still recognisable imprint on local soil. Cr, Cu, Ni and Mn abundance is assumed as an indicator of former Zn processing effect, and inefficient coal combustion that powered smelting as most probable source of Cr, Cu, Ni and Mn immission to environment. Preliminary results on the concentration and distribution of the analysed metals in the soil are presented. Impacts of the metal contamination on the ecosystem have not been widely discussed.

Materials and methods

The scope of research is anthropogenic transformed area in the town of Jaworzno, located in the NE part of the Upper Silesian industrial region, Southern Poland. Many portions of the town have been mined for Zn-Pb ores since 12th century [21] and for coal since 18th century. Centuries-old mining and industrial activity has left numerous traces in the landscape of the town [22]. In the area of present study the exploitation resulted in founding the zinc smelter which started working in the 19th century. It was converted to zinc white (ZnO) plant afterwards and completely ceased in the middle 70's of the 20th century due to the concern of environmental pollution associated with outdated smelting technology [23]. Nowadays, the relics of the zinc historical metallurgic processes are tailings deposited on the old heap, situated in close vicinity of built-up area and community gardens (Fig. 1).

Research was conducted on 4 forest soil profiles of the podzol, which has developed on the fluvio-glacial sediments, and 5 waste samples collected from 3 waste locations (Fig. 1). Each soil profile was divided into separate horizons, what gave 22 soil samples (Table 1). All soil and waste samples, about 2 kg weight each, were collected with small spade and stored in plastic sacks. Samples were collected in September of 2012.

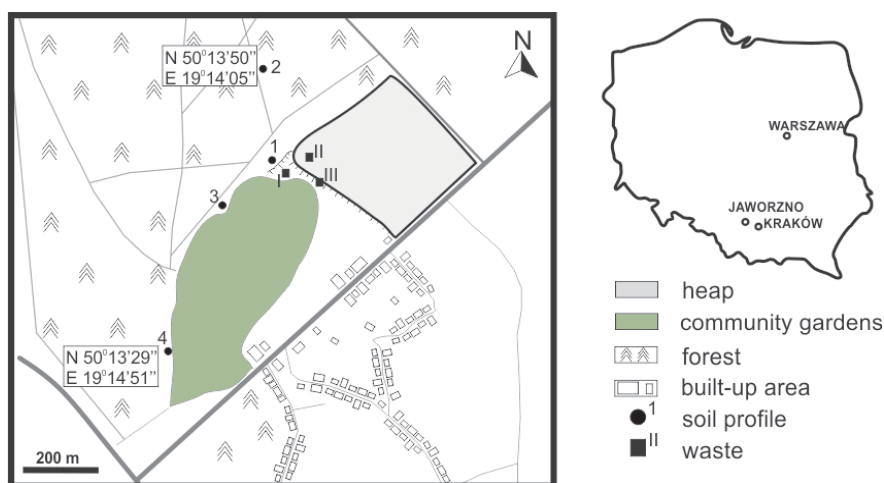


Fig. 1. Location of the study area and sampling sites in Jaworzno

Analyses were preceded by samples oven drying at 105 °C to constant weight, sieving to 2 mm through a stainless steel sieve and milling into fine powder. Soil pH was determined using a 1 : 5 (w/v, g : cm³) ratio of soil/waste and 1 mol · dm⁻³ KCl solution, with pH meter ELMETRON CP-315m.

The phase composition was provided by X-ray diffraction. The analysed material was manually ground in an agate mortar to grain size between 5 and 10 μm. Measurements were carried out in range from 2.5 to 65° 2θ using 100 s time limit and 0.02° 2θ step size. Generator settings were 45 kV and 30 mA. The divergence and antiscatter slits with 1/8° gap were applied. The XRD data were obtained at room temperature and were collected using a Panalytical X'Pert PRO MPD PW 3040/60 diffractometer with a Theta-Theta geometry and X'Celerator strip detector.

Results were processed by HighScore + computer programme of Panalytical company in combination with ICDD, PDF 4+ (version 2012) newest standard base. The mineralogical phase quantitative participations were automatically estimated with Rietveld module of HighScore + programme.

Total contents of Cr, Cu, Ni and Mn were determined in the soil and waste samples. Samples were digested wet in closed system in a mixture of 6 cm³ of concentrated nitric acid (65 % Suprapur) and 2 cm³ of hydrochloric acid (30 % Suprapur). Digestion proceeded with the use of a Multiwave 3000 Microwave Digestion of Perkin Elmer, in two steps according to the program of mineralisation recommended by equipment provider – power: 1400 W, recovery time: 5 min, hold: 25 min in the first step, 10 min in the second, fan speed: 1 in the first step, 3 in the second. After mineralisation the samples were removed to measuring flasks (10 cm³) with 1 % solution of Suprapur nitric acid.

The contents of studied heavy metals in the prepared solution were determined using atomic emission spectrometer ICP-OES Optima 7300 Dual View Perkin Elmer. Each

soil sample was analysed in two replications. If the results of these replications differed one from another by more than 5 %, another two analyses of that sample were conducted.

Results and discussion

The main focus of this study is to give initial information about the contents of Cr, Cu, Ni and Mn in soil and distribution pattern of the metals in soil profiles. Examined forest soil (podzol) developed on the Pleistocene glacial rocks, mainly sand or clay, whereas the waste under study is the material left over after the metallurgical process of Zn and ZnO production.

The pH values measured in the soil varied from 3.85 to 7.59, with median 5.55. The pH value detected for waste material in 1 mol · dm⁻³ KCl solution ranges from 2.83 to 4.28, with median 3.15. It can be concluded that examined materials are ultra acidic to neutral, mostly very strong acidic. According to Kabata-Pendias and Pendias [2], Cr, Cu, Ni and Mn are highly soluble in the acidic soil environment with pH value between 2 and 4.

Mineralogical characterisation of soil profiles and waste materials

Crystalline phases in the topsoil are mainly represented by low-temperature quartz with the highest reflex $d_{110} = 3.343 \text{ \AA}$ and P3₂21 space group (80–98 wt.%). The other minerals identified in this part of soil profile are kaolinite, mica or illite and chlorites. K-feldspars and plagioclases occur there as the accessory minerals. In some samples, larger concentrations of mullite phase (6–15 %) were recognised, accompanied by iron oxides (magnetite, hematite) and rarely akermanite from melilite group. The jarosite-alunite family phases were also documented, which might form by replacing iron sulphides.

The eluvial zone is characterized by similar assemblage of rock-forming minerals and occurring in the same proportion as in the topsoil. The additional phases that appear there are dolomite and trace substances closely related to melilite (akermanite-gehlenite group).

The samples from the illuvial zone can be divided into two types: clayey (samples 1e and 3f) and sandy (samples 2e, 2f and 4d, 4e). In the first type an increase in participation of the clay minerals to over 30 wt.% and the feldspars to 5–7 wt.% is observed. The most frequent clay mineral – kaolinite (about 18 wt.%) is accompanied by mica/illite (12–14 wt.%) and chlorite close to clinochlorite (~10 wt.%). The second type consists of phases similar to those described for eluvial zone with a little addition (3–4 wt.%) of material closely related to microcline. Quartz dominates in both types.

The representation of the jarosite-alunite group phases in diffraction pattern informs about possible oxidation of the iron sulphide minerals in the soil. These sulphides might originate in ore-bearing dolomites, the main source of zinc for Zn-smelting, which naturally have included quantity of iron minerals in their composition.

Apart from natural components of the soil, the mullite, melilite and iron oxides have been identified, which are considered to be anthropogenic. As they are typical

high-temperature minerals, their occurrence can be derived from processes set during Zn-ores smelting.

Phase composition of collected waste is comparable to that in illuvial zone of clayey soil samples; quartz (> 60 wt.%) is there accompanied by clay minerals – mainly kaolinite (~25 wt.%), illite, mica and chlorite (< 10 wt.%). Moreover, Ca and Fe sulphates – gypsum (~2 %), rozenite (~3 %), and phases from alunite-jarosite series (4 % in total) were found in sample I. In material of the sample II, with mineralogical composition similar to that mentioned before, jarosite content is elevated to ~6 %. The III waste sample differs from others because of dolomite (25 %), calcite (~2 %) and hematite (~2 %) presence. It is probable that this material is enriched with ore-bearing dolomite (Zn ore host rock) which contains sizable amount of iron oxides.

Cr, Cu, Ni and Mn contents in soil and waste

Total heavy metal contents in the soils from study area ranged as follows: 21.91–119.32 mgCr · kg⁻¹, 1.40–51.16 mgCu · kg⁻¹, 2.15–36.16 mgNi · kg⁻¹ and 16.33–869.19 mgMn · kg⁻¹, with geometrical means 63.67 mg · kg⁻¹, 8.62 mg · kg⁻¹, 6.13 mg · kg⁻¹ and 71.78 mg · kg⁻¹, respectively (Table 1).

Whereas total contents of the same elements in collected waste samples were comprised in different scopes and ranged as follows: 45.55–67.38 mgCr · kg⁻¹, 19.5–244.74 mgCu · kg⁻¹, 4.96–22.15 mgNi · kg⁻¹ and 30.75–369.11 mgMn · kg⁻¹, with geometrical means 56.06 mg · kg⁻¹, 38.10 mg · kg⁻¹, 6.13 mg · kg⁻¹ and 71.78 mg · kg⁻¹, respectively (Table 2).

The geometrical means of Ni and Mn accumulation are higher in the topsoil than in the tailings, but those of Cr and Cu are the exact opposite.

The geometrical means calculated for the topsoil samples were compared to corresponding values reported by Kabata-Pendias and Pendias [2] for topsoils of the Polish podzols. And medians obtained for the topsoil were correlated with the medians determined by Pasieczna [24] for topsoils in Silesia-Cracow region. The data taken from reference materials [2, 24] were used as regional baseline concentrations. Levels of metal concentrations in the examined topsoil are, except Mn, elevated compared to the baseline values. The Ni contents scarcely exceed mentioned baseline parameters. But the chromium and copper contents are strongly increased, 4–8-fold and 3-fold higher than the baseline concentrations, respectively. Our results are supported by previous research on the Ni contamination of soils in the Olkusz Zn-Pb mining area and in the vicinity of the Tadeusz Sendzimir Steelworks in Krakow [25].

Contents of metals (Cr, Cu, Mn and Ni) in soil seem to be dependent on the distance from the former Zn-smelter. The highest contents of Cu, Ni and Mn were detected close to heap (profile 1), while the lowest ones of Cu, Ni (profiles 2 and 4) and Cr (profile 4) were found in the outermost locations. The highest chromium amount was reported from the profile 2 (for profile localisations see Fig. 1). Similar lateral distribution of heavy metals (Cr, Cu, also Pb, Zn, Cd and As) was observed in other areas impacted by former Zn-smelting *eg* [13, 26].

Table 1

Total heavy metal contents in sampled soils (n = 22)

Soil profile	Sample	Depth [cm]	Cr	Cu	Ni	Mn
			[mg · kg ⁻¹ d.m.]			
1	1a	0–2	107.27	45.49	22.89	673.57
	1b	2–8	97.24	51.16	21.66	340.80
	1c	8–16	71.97	9.74	3.60	35.40
	1d	16–30	62.11	4.85	3.42	32.45
	1e	30–60	85.94	24.30	36.16	869.19
2	2a	0–4	119.32	9.15	5.11	61.96
	2b	4–28	81.85	21.30	6.70	77.05
	2c	28–38	102.65	5.04	3.23	33.65
	2d	38–43	96.98	3.08	3.02	31.43
	2e	43–53	96.14	3.80	4.02	36.15
	2f	53–70	75.54	2.47	3.91	31.90
3	3a	0–2	40.57	21.78	7.66	163.64
	3b	2–10	47.32	38.62	16.72	185.18
	3c	10–20	65.58	24.00	6.79	32.21
	3d	20–28	54.37	2.03	2.15	21.28
	3e	28–40	26.98	1.40	2.64	16.33
	3f	40–65	56.72	5.06	8.71	34.38
4	4a	0–2	24.33	12.21	7.86	166.78
	4b	2–8	21.91	10.82	8.53	132.50
	4c	8–18	62.55	5.63	3.44	40.91
	4d	18–30	61.77	5.63	4.23	79.20
	4e	30–73	79.56	4.10	4.40	60.99
Geometric mean			63.67	8.62	6.13	71.78
Median			68.78	7.39	4.75	50.95
Relative standard deviation [%]			26.81	14.29	8.30	214.25
Geometric mean for studied topsoil			53.62	21.84	11.17	191.73
Median for studied topsoil			47.32	21.78	8.53	166.78
Reference materials						
Median for topsoils in South Poland*			6	7	5	224
Geometric mean for Polish podzol topsoils**			12	8	8	240

Explanations: n – number of analysed samples; * median for topsoils (0–0.3 m) according to geochemical map of Southern Poland (sheets: Slawkow, Olkusz, Nowa Gora, Myslachowice, Chrzanow, Dabrowa Gornicza, Strzemieszyce, Jaworzno and Libiaz) (after 24); ** geometric mean of trace element contents in topsoils of the Polish podzols (after 2).

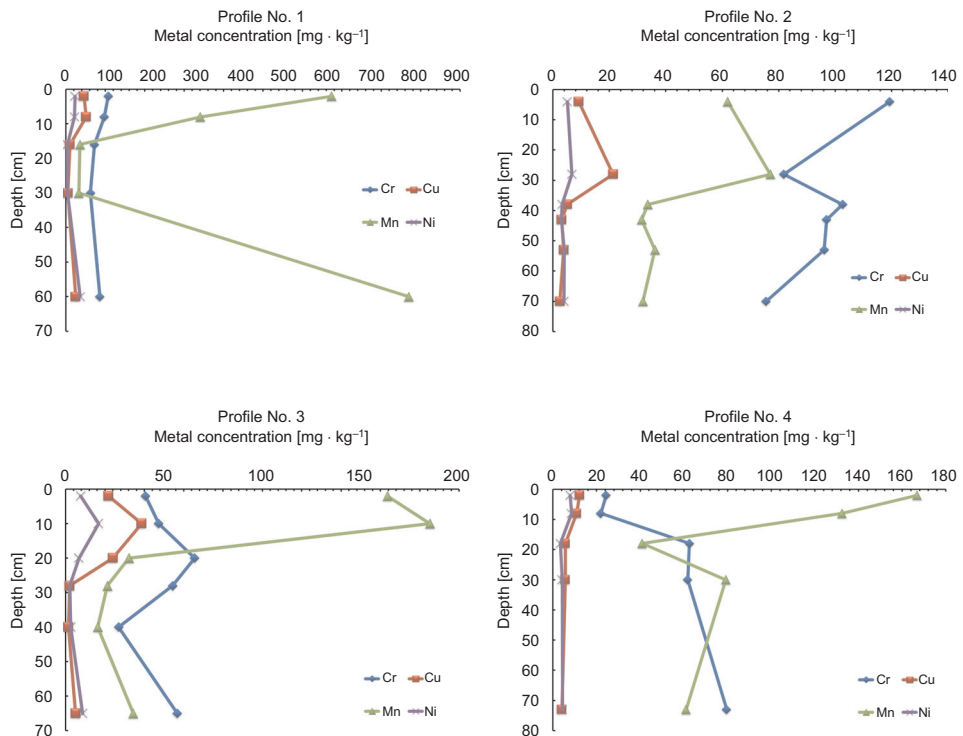
Table 2

Total heavy metal contents in sampled waste (n = 5)

Waste location	Sample	Depth [cm]	Cr	Cu	Ni	Mn
			[mg · kg ⁻¹ d.m.]			
I	Ia	0–10	45.55	20.77	13.11	30.75
	Ib	10–90	54.72	19.50	14.40	42.50
	Ic	90–120	67.38	22.40	4.96	40.73
II		10	60.76	36.14	15.75	101.56
III		50	54.24	244.74	22.15	369.11
Geometric mean			56.06	38.10	6.13	71.78
Median			54.72	22.40	14.40	42.50
Relative standard deviation [%]			7.27	88.22	5.52	128.53

Explanations: see Table 1.

Vertical distribution of examined metal contents in soil is presented in profiles (Fig. 2). Most of the soil profiles exhibits decreasing contents of nickel and copper with

Fig. 2. Vertical distribution of heavy metal contents [mg · kg⁻¹] in studied soil profiles

depth (except profile 2), followed by little enrichment close to bedrock in case of profiles 1 and 3.

Cr distribution similar to that of Cu and Ni is presented only in profile 1 as non-monotonic decrease of Cr level with depth can be observed in profile 2. On the other hand, an increase of Cr content with depth is reflected in profile 4. The biggest enrichment of chromium near the bedrock is seen in profile 3, where Cr concentration can also be considered as growing with depth.

The manganese behaviour is also complicated. Profiles 3 and 4 demonstrate huge depletion of Mn content with depth, while profile 2 shows little growth of Mn quantity in subsoil, and profile 1 reveals strong Mn enrichment close to the bedrock.

According to Ullrich et al [13], distribution pattern exhibited by heavy-metal contents decreasing from topsoil to subsoil generally indicates a non-lithogenic source of the contamination, while higher metal concentrations found at lower depths may reflect the influence of underlying parent rocks or result from downward migration of contaminants related to historic human activity. Evaluating possible reasons of elevated Cr, Cu, Ni and Mn it is important to remind about acidic soil reaction measured for studied soil, which is responsible for heavy metals mobility in environment [2].

Strong correlations are found between studied metals content in soil samples, *eg* Mn and Cu ($r = 0.65$), Ni and Cu ($r = 0.75$), Ni and Mn ($r = 0.95$), while the correlations between Cr and other studied metals are rather weak ($r = 0.19$ – 0.24). The strong correlation coefficients between Ni *versus* Cu and Ni *versus* Mn may indicate genetic relations of these elements to industrial processes.

The smelter emissions, as well as dust wind-blown from factories, tailings and smelter slag dumps are obviously the main point sources of soil pollution [27]. But role of the smelting-related fuel combustion as a source of soil contamination must not be underestimated. About 10–20 % of ash particles are released to the atmosphere because of coal combustion related to mineral processing [2]. The metal contents in the coal ashes are higher than average concentrations in the Earth's crust: 10–1000 mgCr, 50–150 mgCu, 50–10000 mgNi and 200–1200 mgMn · kg⁻¹ what results in large Cr, Cu, Ni and Mn contamination in coal-ash dumps [28] and adjacent sediments [29]. Likewise, high quantities of Ni and Cr could be released to soils during a fast burning of sulphides. Superiority of Cr compared with Ni observed in such soils [30] may document a combined impact of coal combustion and metal smelting processes. Effect of coal burning on the increase of chromium contents in atmosphere and soil is also noted in the vicinities of several power plants in southern Poland [31].

It is reasonable to conclude that metal contamination of the topsoil results from the atmospheric deposition of particles emitted by Pb/Zn smelter. Smelting, converting and fire-refining of base metal concentrates can generate considerable volumes of dust and gases which now are usually passed through electrostatic precipitators to remove almost all of the entrained particulate matter. But in the past, even in 1970's, industrial fumes was not enough purified. And the former, low efficient smelter in Jaworzno needed 18 kg of coal to get 1 kg of clear zinc [32].

Conclusions

The vertical distribution pattern of Cr, Ni, Mn and Cu contents in studied profiles suggests an anthropogenic origin of soil contamination. High concentrations of analysed metals together with occurrence of man-made high-temperature phases point to smelting-related fuel combustion as a possible source of the metals in soil. Lateral dispersal of the metals, from the highest concentrations detected close to heap to the lowest found in the outermost profiles enables locating the former Zn-smelter in the positive anomaly center.

The soil is still polluted by hazardous trace elements (HTEs) even though the Zn smelting and the ZnO production became closed more than forty years ago. Contents of chromium, copper and nickel in the examined topsoil are up to 8-fold elevated compared to the baseline values, and strong acidity at the site activates Cr, Cu, Ni and Mn high solubility. Thus, soil environment has been changed to dangerous for humans, especially due to close proximity of abandoned industry to built-up and recreation areas as well as community gardens.

Sequential extraction of trace elements should be done in the next step of the research to precise heavy metals behaviour in the soil. Potential harm of the pollutants to eco-environment and human health in the vicinity of the zinc historical industry area in Jaworzno should also be examined in greater detail.

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ZANIECZYSZCZENIE GLEBY METALAMI CIĘŻKIMI ZWIĄZANE Z HISTORYCZNYM HUTNICTWEM CYNKU W JAWORZNIE

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Abstrakt: Przeprowadzono wstępne badania zanieczyszczenia metalami ciężkimi (Cr, Cu, Ni i Mn) w 22 próbkach pobranych z 4 profili leśnych gleb bielcowych oraz 5 próbkach odpadów pohnicznych pobranych z 3 punktów w rejonie historycznego hutnictwa cynku w Jaworznie (południowa Polska). Wykonano pomiary pH oraz analizy XRD. Zawartość pierwiastków śladowych oznaczono, stosując optyczny spektrometr plazmowy (ICP-OES) po wcześniejszym zmineralizowaniu próbek w stężonym HNO₃ (65 % Suprapur) i HCl (30 % Suprapur). Badane materiały miały odczyn od ekstremalnie kwaśnego do obojętnego, w większości bardzo kwaśny. Całkowita zawartość pierwiastków śladowych w badanych glebach wahała się w szerokim zakresie: od 21,91 do 119,32 mgCr, od 1,4 do 51,16 mgCu, od 2,15 do 36,16 mgNi i od 16,33 do 869,19 mgMn · kg⁻¹. W materiale odpadowym zawartości badanych pierwiastków wynosiły: 45,55–67,38 mgCr, 19,5–244,74 mgCu, 4,96–22,15 mgNi i 30,75–369,11 mgMn · kg⁻¹. W badaniach określono również pionową zmienność zawartości metali w poszczególnych profilach glebowych. Wykryte zawartości metali ciężkich świadczą o silnym zanieczyszczeniu gleb. Wskazano na dawną działalność hutniczą jako na źródło tego zanieczyszczenia, które może stanowić zagrożenie dla mieszkańców, ze względu na bliskie sąsiedztwo zamkniętej huty z obszarami zabudowanymi i rekreacyjnymi oraz ogrodami działkowymi.

Słowa kluczowe: hutnictwo cynku, metale ciężkie, zanieczyszczenia gleby

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EMISSION OF VOLATILE FLUORINE COMPOUNDS FROM PARTIALLY ACIDULATED PHOSPHATE ROCKS PRODUCTION PROCESS

EMISJA LOTNYCH ZWIĄZKÓW FLUORU Z PROCESU OTRZYMYWANIA FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

Abstract: Emission of volatile fluorine compounds is considered to be the major environmental concern of the phosphate fertilizers manufacturing process. The results of presented studies indicates that the use of PAPR technology as an alternative to conventional superphosphatic fertilizers reduces F⁻ total emission. For the assumed production capacity of 800 Mg/day of PAPR products a decrease in η_{PAPR} value from 1.0 (SSP) to 0.3 causes a reduction in F⁻ by average: 6045 \rightarrow 1675 kg/day and 1545 \rightarrow 506 kg/day for H₂SO₄ and H₃PO₄ respectively as the mineral acids used for acidulation process, while decrease in η_{PAPR} value from 1.0 (SSP) to 0.5 causes a reduction in F⁻ by average: 6045 \rightarrow 1865 kg/day and 1545 \rightarrow 660 kg/day for H₂SO₄ and H₃PO₄, respectively. Reducing the F⁻ content improves environmental and economic profile of the installation, limits the amount of resulting silica, and allow a reduction in off-gas flow intensity, or spraying density.

Keywords: phosphate fertilizers, partially acidulated phosphate rocks (PAPR), volatile fluorine compounds

Introduction

Manufacturing of phosphate fertilizers involves emission of significant amount of gases, which consist particularly of a mixture of HF and SiF₄, causing the problem of acute phytotoxicity near the fertilizer manufacturing plants [1, 2]. Furthermore, the contamination level of fluoride in fertilizer formulations can reach up to 3 % by weight, what may cause the risk of increased concentrations of fluoride in the soil to phytotoxic values at the long-term application (for example SSP application of 10–30 kgP · ha⁻¹ · year⁻¹ cause introduction into the soil of 1–6 kgF · ha⁻¹ · year⁻¹) [3]. It is strictly dependent on

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the method of purification of waste gases collected from the mixer and reaction den, which typically are scrubbed by a two-stage fan system comprising scrubber, a packed absorption column – sprayed with fluosilicic acid solution and water separator cyclone. Moreover, in conventional superphosphatic technology, periodically stored fluosilicic acid, evolved from the absorption unit of fluorinated gases, is recycled to the powder fertilizer production, where is used as a substitute for the phosphate rock acidulation reaction. It concurrently reduces the consumption of sulfuric or phosphoric acid, and the cost of H_2SiF_6 neutralization [4, 5]. However, this loads fertilizer products with additional fluoride amount, generating a risk of accumulation of its toxic levels in crops [6]. PAPR (*Partially Acidulated Phosphate Rock*) technology seems to be a sustainable solution for the production of phosphate fertilizers in terms of these aspects. It is based on the use of portion of stoichiometric amount of sulfuric acid, phosphoric acid or mixtures thereof, required for the complete dissolution of phosphate rock apatitic structure to form a water-soluble $\text{Ca}(\text{H}_2\text{PO}_4)_2$ [7–11]. Given the current economy, it is profitable and at the same time reduces the adverse environmental aspects. The unit which defines fertilizer formulations of PAPR-type is a degree of PAPR stoichiometric norm (η_{PAPR}) expressed as the ratio of amount of mineral acid actually used to the stoichiometric quantity of acid required to fully acidulate a particular phosphate rock to single superphosphate (SSP):

$$\eta_{\text{PAPR}} = \frac{\eta_{\text{min.ac.}}^{\text{a}}}{\eta_{\text{min.ac.}}^{\text{s}}}$$

where: η_{PAPR} – degree of PAPR stoichiometric norm,
 $\eta_{\text{min.ac.}}^{\text{a}}$ – amount of mineral acid actually used in the acidulation process,
 $\eta_{\text{min.ac.}}^{\text{s}}$ – the stoichiometric quantity of acid required to fully acidulate a particular phosphate rock to SSP.

Conventional SSP in this convention reach $\eta_{\text{PAPR}} = 1$. The η_{PAPR} value determines the content of both available and insoluble phosphate forms. Insoluble forms represent mainly unacidulated parts of phosphate rock. After application to the soil, chemical processes and microbial mineralization take place and turn them into a reserve of phosphorus compounds [12].

Materials and methods

Fertilizer preparations of a PAPR-type were obtained in the model-type Atlas apparatus (Syrris Ltd.) consisting of the following units:

- The ellipsoid bottom experimental reaction vessel made of Teflon, developed with working volume of approximately 0.8 dm^3 , equipped with a cover with openings that enabled feeding the batch;
- Mechanically controlled stirrer IKA RW 28 BASIC;

– Volatile fluorine compounds absorption system in an alkaline solution (NaOH 1 M) comprising a laboratory scrubber with a capacity of 500 cm³, in series with a reaction vessel containing 250 cm³ of a solution of an alkali;

– Diaphragm vacuum pump N86KN.18 Laboport[®] combined with absorption system forcing the process gas flow.

Technical specification of applied apparatus and a process parameters (Fig. 1) enabled in a high degree to imitate the unit processes that occur in the technological line to manufacture single superphosphate (SSP).

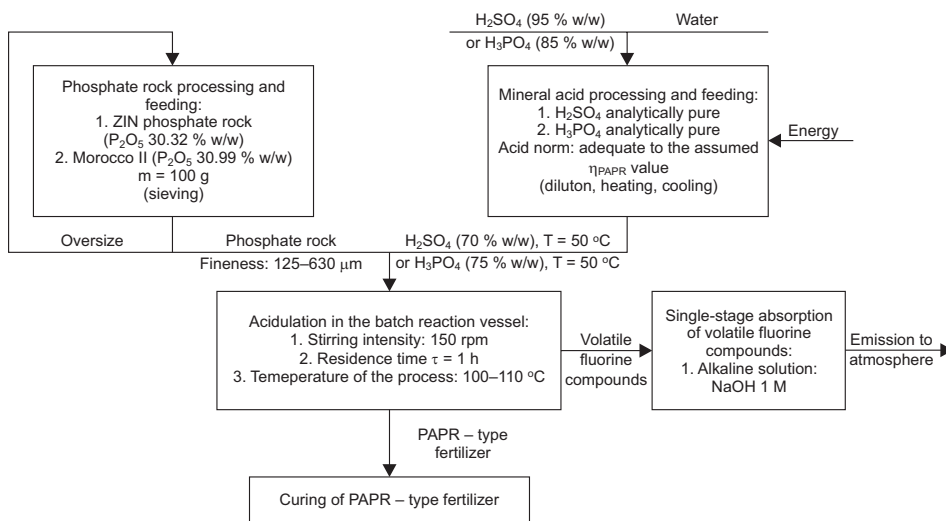


Fig. 1. Schematic diagram of laboratory installation for production of PAPR-type fertilizer formulations

“Morocco II” and “ZIN” phosphate rock samples were used for investigations. The selected raw materials have been widely used by the national phosphate fertilizer manufacturers. Morocco’s enormous measured phosphate rock resources are hosted in upper cretaceous, palaeocene and eocene sediments. Sequences comprising clays, marls, limestones and cherts contain several phosphate-rich beds. Phosphate rock mining centres are operated by Office Chérifien des Phosphates (OCP). Moroccan phosphate rock are enriched by simple mechanical processes [13]. “ZIN” phosphate rocks are being extracted from deposits located in the eastern desert Nagev in Israel. As a commercial product is available in processed form as a result of hydraulic and washing beneficiation [14]. The results of chemical analysis of tested phosphate rocks samples are summarized in Table 1.

The free F⁻ ions content in the investigated samples was determined by potentiometric method using a fluoride ionplus sure-flow solid state combination electrode connected with the multi-parameter laboratory meter 5-STAR (Thermo Scientific Orion). The device allowed the measurement of the concentration of free fluoride ions in range of mg/dm³ against the calibration curve. Calibration of the equipment was

Table 1

Chemical composition of tested phosphate rocks samples

Parameter	Unit	Results for given type of phosphate rock	
		Morocco II	ZIN
P soluble in mineral acids	P ₂ O ₅ % w/w	30.99	30.32
P soluble in 2 % citric acid (20 g per dm ³)	P ₂ O ₅ % w/w	2.02	5.69
P soluble in 2 % formic acid (20 g per dm ³)	P ₂ O ₅ % w/w	1.49	5.52
P soluble in neutral ammonium citrate	P ₂ O ₅ % w/w	2.91	3.66
P water-soluble	P ₂ O ₅ % w/w	insoluble	insoluble
F	% w/w	3.44	3.61
CaO	% w/w	54.80	49.59
Al ₂ O ₃	% w/w	0.12	0.24
Fe ₂ O ₃	% w/w	0.41	0.40

performed based on the measurement of the potential of standard solutions with concentrations of 100, 250 and 500 mg/dm³ F⁻. The procedure for measuring the concentration of F⁻ ions, developed on the basis of Al-Othman's research, was shown schematically in Fig. 2 [17].

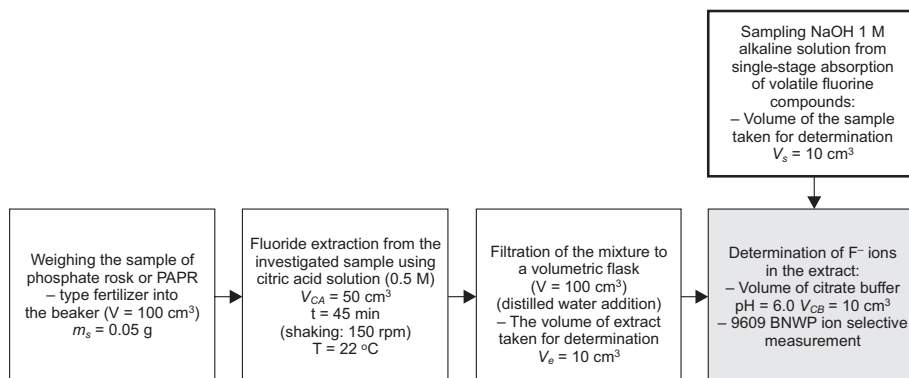


Fig. 2. Schematic diagram of the procedure for determination of the F⁻ ions in the examined samples

Results and discussion

Table 2 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of Morocco II phosphate rock dissolution using PAPR technique with H₂SO₄. The results were recalculated for an industrial plant with the production capacity of the assumed 800 Mg of PAPR-type fertilizer product per day.

In the course of investigations it was found that the amount of volatile fluorine compounds emitted from the PAPR manufacturing system increases with higher values of η_{PAPR} along. The reference product $\eta_{\text{PAPR}} = 1$ was characterized by the maximum level of emissions of volatile fluorine compounds, revealing the highest absorption

Table 2

A simplified material balance for the process of absorption of the volatile F compounds from the products of Morocco II phosphate rock acidulation by PAPR technique using H₂SO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (Morocco II) consumption	Mg/day	772.0	699.6	626.8	571.9	509.0
F ⁻ content in phosphate rock	Mg/day	26.6	24.1	21.6	19.7	17.5
F ⁻ content in product	Mg/day	26.1	21.4	18.7	17.8	13.7
F ⁻ total emission	kg/day	480.0	2630.0	2840.0	1910.0	3750.0
F ⁻ organised emission	kg/day	237.4	182.6	188.1	358.0	522.3
F ⁻ unorganised emission	kg/day	242.6	2447.4	2651.9	1552.0	3227.7
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	52.8	50.8	59.7	78.9	86.3
F ⁻ removal	kg/day	125.4	92.7	112.2	282.5	450.5
Waste F ⁻ emission	kg/day	111.9	89.9	75.8	75.5	71.8

performance and concurrently the lowest F⁻ content in the fertilizer product. Analysis of the absorption performance results for the mixture of HF and SiF₄ showed a declining trend with decreasing values of η_{PAPR} in the laboratory conditions. This may be caused by too low flow rate of exhaust gases which achieves the optimum value of approximately 30000 Nm³/h in an industrial conditions. The rapid growth of emissions of volatile fluorine compounds was observed for fertilizer products of $\eta_{\text{PAPR}} > 0.5$. Table 3 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of ZIN phosphate rock dissolution using PAPR technique with H₂SO₄.

Table 3

A simplified material balance for the process of absorption of the volatile fluorine compounds from the products of ZIN phosphate rock acidulation by PAPR technique using H₂SO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (ZIN) consumption	Mg/day	774.1	693.7	636.2	583.2	516.9
F ⁻ content in phosphate rock	Mg/day	27.9	25.0	22.9	21.1	18.7
F ⁻ content in product	Mg/day	27.3	24.3	22.1	18.5	10.3
F ⁻ total emission	kg/day	670.0	720.0	890.0	2570.0	8340.0
F ⁻ organised emission	kg/day	195.5	174.1	156.2	169.4	550.0
F ⁻ unorganised emission	kg/day	474.5	545.9	733.8	2400.6	7790.0
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	55.6	54.8	53.4	60.1	87.4
F ⁻ removal	kg/day	108.8	95.4	83.3	101.8	480.7
Waste F ⁻ emission	kg/day	86.7	78.7	72.8	67.7	69.3

A comparison of material balances of volatile fluorine compounds for both phosphate rocks made us able to observe that the F^- content in PAPR-type fertilizer products acidulated with H_2SO_4 of η_{PAPR} values in range of 0.1–0.7 were higher for ZIN phosphate rock sample. This correlates with the higher content of F^- in the raw mineral of approximately 0.5 % w/w against Morocco II phosphate rock. Waste F^- emission values were lower by 5–15 % when ZIN phosphate rock was applied for the dissolution process, particularly for fertilizer products of η_{PAPR} values in range of 0.1–0.5. Other parameters indicated comparable values.

In order to determine the influence of the type of mineral acid applied in the acidulation process (H_2SO_4 or H_3PO_4 in this case) on F^- emission profile, the PAPR-type fertilizers were also manufactured using H_3PO_4 . It was crucial to determine whether there is resemblance in F^- content trends in the particular range of the η_{PAPR} values of PAPR products obtained in the laboratory conditions. Table 4 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of Morocco II phosphate rock dissolution using PAPR technique with H_3PO_4 .

Table 4

A simplified material balance for the process of absorption of the volatile F compounds from the products of Morocco II phosphate rock acidulation by PAPR technique using H_3PO_4

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (Morocco II) consumption	Mg/day	727.8	583.4	528.9	431.3	359.7
F^- content in phosphate rock	Mg/day	25.0	20.1	18.2	14.8	12.4
F^- content in product	Mg/day	24.6	19.8	17.9	14.2	10.7
F^- total emission	kg/day	480.0	230.0	280.0	680.0	1660.0
F^- organised emission	kg/day	268.6	178.2	116.1	90.1	79.5
F^- unorganised emission	kg/day	211.4	51.8	163.9	589.9	1580.5
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	71.5	64.6	51.0	50.7	52.5
F^- removal	kg/day	192.2	114.3	59.2	45.7	41.7
Waste F^- emission	kg/day	76.4	63.9	56.9	44.4	37.8

Potentiometric analysis for fluoride content determination revealed that the amount of volatile fluorine compounds emitted from the laboratory PAPR manufacturing system based on H_3PO_4 increases with higher values of η_{PAPR} along, likewise in PAPR products acidulated with H_2SO_4 . Moreover, the reference product $\eta_{PAPR} = 1$ was characterized by the maximum level of emissions of volatile fluorine compounds and concurrently the lowest F^- content in the fertilizer product. However, unlike PAPR product acidulated with H_2SO_4 , it had the lowest absorption performance result for the

mixture of HF and SiF₄ while indicating an upward trend with decreasing values of η_{PAPR} in the laboratory conditions. Table 5 depicts the simplified material balance for the absorption of volatile fluorine compounds evolved from the products of ZIN phosphate rock dissolution using PAPR technique with H₃PO₄.

Table 5

A simplified material balance for the process of absorption of the volatile fluorine compounds from the products of ZIN phosphate rock acidulation by PAPR technique using H₃PO₄

Parameter	Unit	Results for given type of fertilizer product depending on η_{PAPR} value				
		0.1	0.3	0.5	0.7	1.0
Fertilizer output	Mg	800.0				
Phosphate rock (ZIN) consumption	Mg/day	726.9	603.5	514.0	445.2	376.4
F ⁻ content in phosphate rock	Mg/day	26.2	21.8	18.6	16.1	13.6
F ⁻ content in product	Mg/day	25.5	20.9	17.5	14.9	12.2
F ⁻ total emission	kg/day	720.0	910.0	1040.0	1190.0	1430.0
F ⁻ organised emission	kg/day	153.0	130.7	110.5	98.6	84.7
F ⁻ unorganised emission	kg/day	567.0	779.3	929.5	1091.4	1345.3
Gas flow rate	Nm ³ /h	0.4	0.4	0.4	0.4	0.4
Absorption performance	%	52.5	52.4	50.9	52.1	52.0
F ⁻ removal	kg/day	80.3	68.5	56.3	51.4	44.0
Waste F ⁻ emission	kg/day	72.7	62.2	54.2	47.2	40.7

The F⁻ content in PAPR-type fertilizer products acidulated with H₃PO₄ were higher for ZIN phosphate rock sample in the whole spectrum of η_{PAPR} values, just as in the case of products acidulated with H₂SO₄. Again, it may be correlated with the higher content of F⁻ in the raw mineral of approximately 0.5 % w/w against Morocco II phosphate rock. Waste F⁻ emission values were virtually at the same levels for both phosphate rocks, whereas the average values were significantly lower in comparison with PAPR fertilizer formulations manufactured using H₂SO₄. Other parameters indicated comparable values.

Conclusions

The study indicates that the use of PAPR technology as an alternative to conventional superphosphatic fertilizers reduces F⁻ total emission. For the assumed production capacity of 800 Mg of PAPR fertilizer products per day a decrease in η_{PAPR} value from 1.0 (SSP) to 0.3 causes a reduction in F⁻ by average: 1545 → 506 kg/day and 6045 → 1675 kg/day for H₂SO₄ and H₃PO₄ respectively as the mineral acids used for acidulation process, while decrease in η_{PAPR} value from 1.0 (SSP) to 0.5 causes a reduction in F⁻ by average: 6045 → 1865 kg/day and 1545 → 660 kg/day for H₂SO₄ and H₃PO₄ respectively. The influence of the type of mineral acid applied in the

acidulation process (H_2SO_4 or H_3PO_4 in this case) on F^- emission profile was particularly shown by indicating an upward trend in the absorption performance results for the mixture of HF and SiF_4 with decreasing values of η_{PAPR} for PAPR products acidulated with H_3PO_4 . Furthermore average waste F^- emission values were significantly lower unlike in PAPR fertilizer formulations manufactured by using H_2SO_4 for acidulation process. A reasonable conclusion to draw from these results is that F^- emission is highly dependent on the amount of phosphate rock feed into the manufacturing process. Thus, in case of PAPR products acidulated with H_3PO_4 the amount of volatile fluorine compounds evolved will be lower for particular η_{PAPR} value for the specified mass unit as the part of P_2O_5 is introduced with H_3PO_4 . Despite improvement of environmental protection issues, the lower content of F^- , which leads concurrently to reduce the amount of resulting silica, may allow also a reduction in off-gas flow intensity, or spraying density, which could potentially lead to decrease the cost of purification of 1 m^3 of the off-gas.

Acknowledgements

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EMISJA LOTNYCH ZWIĄZKÓW FLUORU Z PROCESU OTRZYMYWANIA FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

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Abstrakt: Emisja lotnych związków fluoru jest uważana za podstawowe zagrożenie środowiskowe procesów wytwarzania nawozów fosforowych. Rezultaty przeprowadzonych badań wskazują, że stosowanie technologii PAPR jako alternatywy dla konwencjonalnych nawozów superfosfatowych, powoduje zmniejszenie emisji całkowitej F^- . Dla założonej zdolności produkcyjnej 800 Mg/dobę produktów nawozowych typu PAPR obniżenie wartości η_{PAPR} z 1,0 (SSP) do 0,3 powoduje redukcję F^- średnio: 6045 \rightarrow 1675 kg/dobę oraz 1545 \rightarrow 506 kg/dobę dla odpowiednio H_2SO_4 i H_3PO_4 jako kwasów mineralnych zastosowanych w procesie roztwarzania; podczas gdy obniżenie wartości η_{PAPR} z 1,0 (SSP) do 0,5 powoduje redukcję F^- średnio: 6045 \rightarrow 1865 kg/dobę oraz 1545 \rightarrow 660 kg/dobę odpowiednio dla H_2SO_4 i H_3PO_4 . Obniżenie zawartości F^- poprawia profil środowiskowy oraz ekonomiczny instalacji, prowadząc jednocześnie do ograniczenia ilości powstającej krzemionki, pozwalając na zmniejszenie natężenia przepływu gazów odlotowych lub gęstości zraszania.

Słowa kluczowe: nawozy fosforowe, fosforyty częściowo rozłożone (PAPR), lotne związki fluoru

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INVESTIGATIONS OF BIO-DRYING PROCESS OF MUNICIPAL SOLID WASTE

BADANIA BIOSUSZENIA ODPADÓW KOMUNALNYCH

Abstract: Operation analysis of the mechanical-biological stabilization reactor was presented. Municipal waste undergoes mechanical pretreatment and then the fraction 0–80 mm rich in organic matter is treated by oxidic method in the reactor. Results of investigations of raw MSW (0–80 mm) and stabilat (0–20 mm, 20–80 mm) which are the resulting material after the 7th days bio-drying processes, were discussed. The loss of ignition (LOI), humidity, pH, the amount of sulfur, chlorides, heavy metals and the biologically stable state are the main investigated parameters. To evaluate the material stabilization, the determination of the O₂ uptake and CO₂ production was measured. The results allowed to evaluate the work effectiveness of the industrial reactor constructed for MSW treatment. The experiments were led using an OXYMAX respirometer ER-10 (Columbus Instruments), an ion chromatograph 883 Basic IC plus, spectrometer with plasma ICP.

Keywords: mechanical-biological stabilization, biodrying MSW, respirometry

Introduction

The *mechanical-biological treatment* (MBT) is an integrated process which includes: the mechanical processing (crushing, screening, separation and compaction) [1] and the biological (aerobic and anaerobic methods) [2]. MBT systems are led to treatment *municipal solid waste* (MSW) for reducing the amount of waste going to landfill. As a result, this method provides the energy recovery (energy, electricity) or the material recovery (organic recycling). Generally, two aerobic methods are available: the composting and the *mechanical biological stabilization* (MBS) also called a biodrying [3]. The MBS is a relatively new direction. Produce of *residual derived fuel* (RDF) is

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the main idea of biodried technologies. Alternative option for using MBS is stabilization/preparing of waste going to landfills. Preparing waste for disposal is a result of law requirements [4].

Evaluation work effectiveness of industry reactor for biostabilization organic fraction was the main aim of the analysis. The reactor is an element of technology for mechanical-biological treatment of waste (MBT).

Mechanical-biological stabilization plant

The analyzed MBS technology includes: screenings, the reactor, module of active aeration with stove and finally bio-filter which removes odors. The scheme of biodrying technology was presented in Fig. 1. The reactor has rectangular shape and was made of galvanized steel. The reactor treats the 0–80 mm fraction of MSW. The biodrying bed is approximately 2/3 of total height of the reactor. The retention time is 7–14 days. The downcast ventilator (air flow) and the exhaust ventilator (moisture removal) work continuously. Engine power of the downcast ventilator is 7.5 kW. The maximum amount of air flow to the reactor is 4500 m³/h. Exhaust ventilator with motor power 4.0 kW, which is both moisture removal and air flow for biofilter, works with a yield of 3000 m³/h.

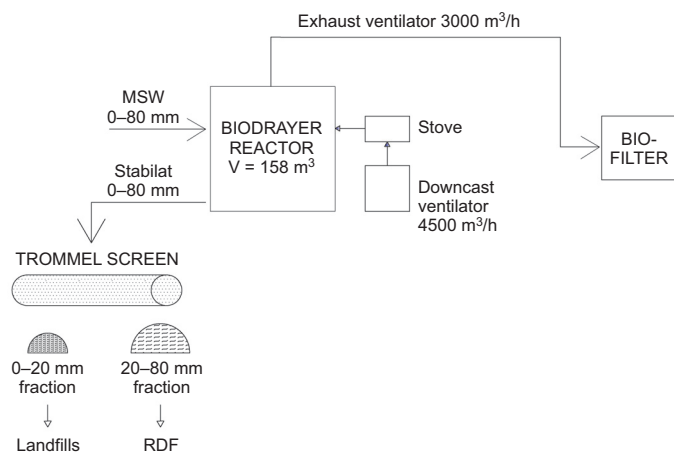


Fig. 1. The scheme of MBS plant with active aeration for stabilization MSW

The MBS idea involves the separation of waste after biological drying to fraction 20 mm and 20–80 mm. According to the technology concept, dried fraction 0–20 mm (code 19 12 12 – wastes from mechanical treatment) goes to the landfill. Fraction 20–80 mm (code 19 12 10 – combustible waste, refuse derived fuel) is treated by the thermal methods, which is in accordance with § 5.6. Regulation [5].

In connection with the technology concept, which assumes that fraction 0–20 mm are going to landfill, measurement of loss on ignition was made. The results were compared with requirements of the Minister of Economy [4]. Biodried 0–20 mm fraction can be

classified with code 19 12 12*. According to the Regulation [4] waste code 19 12 12 may be taken to a landfill for non-hazardous and inert waste if they fulfill the requirements set out in the annex 4 [4]:

- loss of ignition (LOI) < 8 % d.m.,
- total carbon organic (TOC) < 5 % d.m.,
- heat of combustion max. 6 MJ/kg d.m.

Based on § 7 [4] these criteria will be obliged from 1.01.2016, however, selective control parameters of waste going to landfill will be realized, how difficult it is to fulfill these stringent parameters. These requirements will help to reduce the amount of landfilled waste significantly.

The criteria for stabilat

MBS technologies treated the municipal solid waste. Process of biological drying should take place in closed reactor with active aeration for minimum 7 days, which is in accordance with § 4.4. Regulation [5]. Finally, waste after MBP technologies should fill one of following criteria [5]:

- Loss of ignition (LOI) < 35 % dry mass, and the amount of total carbon organic (TOC) < 20 % d.m., or
- The loss of organic matter in processes before and after stabilization should be higher than 40 % d.m., or
- Respiration Activity $RA_4 < 10 \text{ mgO}_2/\text{g d.m.}$

In order to assess the correctness of MBS process, there were analyzed LOI and respiration activity of 0–20 mm fraction and LOI of 20–80 mm fraction.

There are three types of measurement biological stability. The reactivity/stability of the MBT products can be determined by aerobic and anaerobic methods [6]. The aerobic indices are based on respiration techniques, while the anaerobic on biogas production. Respiration techniques are based on the measurement of the loss of O_2 in the reactor and are the most accepted because of the precise information about the real biological activity of the samples [6]. One of respirometric parameter is RA_4 , that presents microbiological oxygen consumption for 4 days. RA_4 parameter determines the ability of waste for further biological decomposition [3]. The respiration activity is measured in an oxygen atmosphere, for a 30 g minimum sample weight and the humidity of 40–50 % [6]. The amount of oxygen consumed by microorganisms can be determined by methods: the static (without a continuous supply of air during the assay) and the dynamic (with a continuous supply of air). The most popular equipment for determining RA_4 are Sapromat and Oxitop (static method). In these equipments may occur the anaerobic atmosphere and disturbing of the final result. Moreover, products of the biological decomposition led to next mistake which equipment register as CO_2 . Micro-Oxymax and Costech are respirometry equipment working basing on dynamic

* Other wastes (including mixtures of materials) from mechanical treatment of wastes other than those mentioned in 19 12 11.

methods [7–9]. Figure 2 presents the test stand for dynamic measurement O₂ uptake and CO₂ production.

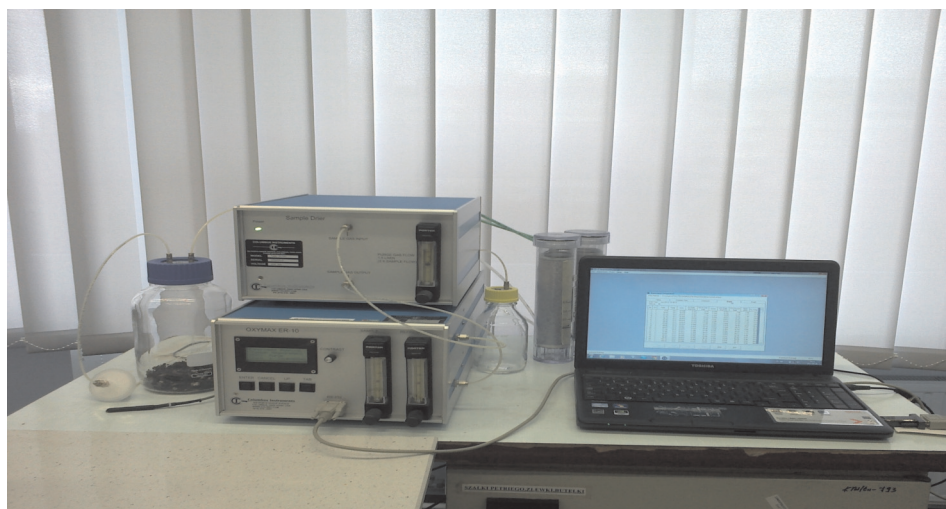


Fig. 2. The test stand for measuring biological activity – respirometer Oxymax ER-10

Materials and research methods

Investigations included two phases: the study of waste going to the stabilization and testing of the biodried waste MBS, which called stabilat. Table 1 and 2 present the characteristic parameters of investigated materials. The probes of 0–80 mm MSW fraction were taken according to the standard procedure – the method of quartering [10]. Investigations of humidity were determined by weight loss mass of dried waste at 105 °C [11]. The weights of the dried waste samples were approximately 1000 g. Measurement of loss on ignition was determined by 5 g samples according Polish Standards [12].

The basis for the analysis of chlorides, sulphates and heavy metals Cd, Cu, Cr, Ni, Pb, Zn was a procedure for preparing the water extract of solid wastes according to procedure presented in Fig. 3 [13]. Samples taken to water extraction tests were in natural size. The liquid used to prepare the extraction test was distilled water. Testing procedure was carried out at room temperature.

Three extracts should be treated separately. The amount of determined element in first water extract should be calculated from formula [13]:

$$q_1 = \frac{V_1 \cdot c_1}{m} \quad (1)$$

where: q_1 – the amount of determined element [g/kg d.m.],
 V_1 – volume of water extract in first step [cm³],

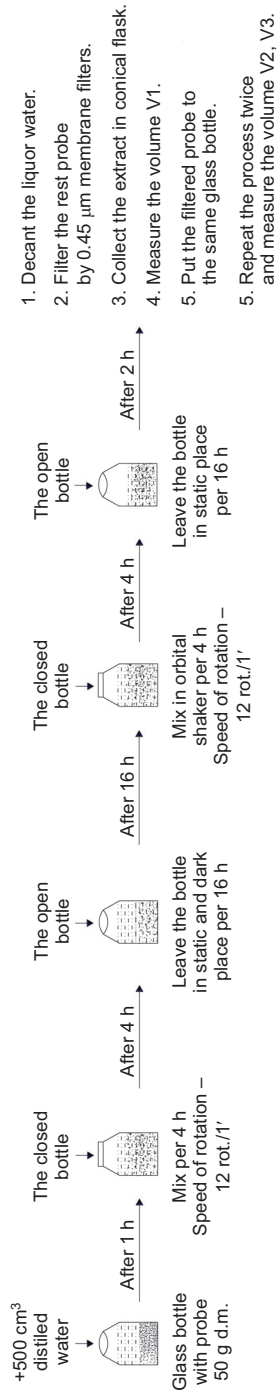


Fig. 3. The procedure used for water extraction test from waste (according to [13])

c_1 – concentration of determined element [mg/cm³],
 m – weight of dry mass [g].

The amount of determined element in water extract in second step should be calculated from formula [13]:

$$q_2 = \frac{V_0 \cdot c_2}{m} \quad (2)$$

where: q_2 – the amount of t determined element [g/kg d.m.],
 V_0 – volume of water used to extract in second step [cm³],
 c_2 – concentration of determined element [mg/cm³],
 m – weight of dry mass [g].

The amount of determined element in water extract in third step should be calculated from formula [13]:

$$q_3 = \frac{V_0 \cdot c_3}{m} \quad (3)$$

where: q_3 – the amount of determined element [g/kg d.m.],
 V_0 – volume of water used to extract in third step [cm³],
 c_3 – concentration of determined element [mg/cm³],
 m – weight of dry mass [g].

The total amount of determined element in g/kg d.m. should be calculated from formula [13]:

$$Q = q_1 + q_2 + q_3 \quad (4)$$

The elutes obtained in above mentioned procedure were the object further investigations.

The amounts of anions were measured by ion chromatograph 883 Basic IC plus, while the heavy metals by ICP plasma spectrometer.

The biological stability was determined by dynamic tests using a respirometer Oxymax ER-10. The respirometer took a series of gas measurements with 5 minutes interval, recording the net increase or decrease in the concentration of the monitored gases. Research sample weight for 0–80 mm fraction was 100 g, input moisture 41.39 %, shredding < 9 mm.

The idea of technology is based on biological stabilization municipal solid waste 0–80 mm fraction with continuous aeration for 7 days. After processes the stabilats were directed to a rotary screen. Two output streams 0–20 mm and 20–80 mm were the separated products. Stabilized fraction 0–20 was tested analogously to the 0–80 mm fraction. The oxygen uptake and production of carbon dioxide were measured only for 0–20 mm fraction with parameters: probe mass 300 g, input moisture 42 %, shredding < 9 mm.

Results

Average values of moisture, loss on ignition (LOI), chlorides and sulphates anions are presented in Table 1. Results presented in Table 1 were averages from three investigations.

Table 1

Humidity, LOI in probes and chlorides, sulphates ,pH in elutes from waste taken before and after 7-days stabilization

Sample	Fraction [mm]	Investigations directly in waste probes		Investigations in extraction test		
		Humidity [%]	Loss of ignition LOI [% d.m.]	Chlorides Cl ⁻ [mg/kg d.m.]	Sulphates SO ₄ ²⁻ [mg/kg d.m.]	pH
Before stabilization	0–80	45.00	62.10	1135.41	1347.83	7.39
After stabilization	0–20	30.48	24.80	2339.20	7614.69	7.5
After stabilization	20–80	35.61	49.20	458.08	1416.26	7.6

Table 2 summarizes the data respiration activity of the raw MSW 0–80 mm fraction and the 0–20 mm stabilized fraction. Respirometric activity was examined for stabilat 0–20 to verify work of the reactor that must achieve requirement level $AT_4 < 10$ mgO₂/g d.m. [5]. The oxygen consumption measured for 4 days for fraction 0–80 mm was 47.85 mgO₂/g d.m. Results of analysis were compared with law requirements for waste disposal [5].

Table 2

The measurement gases for 0–80 mm and 0–20 mm fractions after bio-drying process in industrial reactor

Fraction [mm]	Accumulative consumption O ₂ [mg/96 h]	Accumulative production CO ₂ [mg/96 h]	Average ratio CO ₂ /O ₂ [-]	Consumption O ₂ /96 h [mgO ₂ /g d.m.]
0–80	2870.89	3578.19	1.16	47.85
0–20	1633.23	1939.48	1.04	8.17

Figure 4 and 5 illustrate values of heavy metals tested by spectrometry methods in elutes. The following wavelengths in [nm] were taken to analyze the elements:

- Cd 228.802
- Cu 327.393
- Cr 267.716
- Ni 231.604
- Pb 220.353
- Zn 206.200

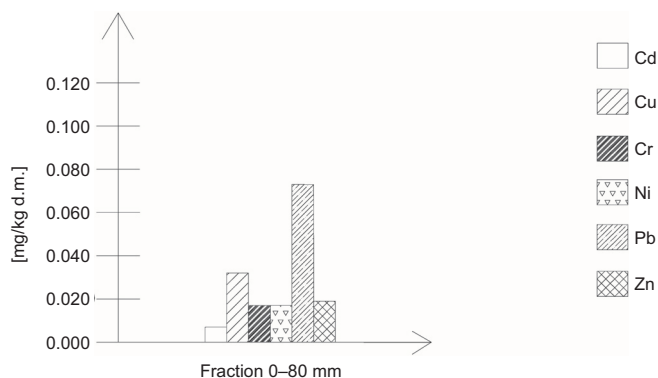


Fig. 4. Heavy metals analysis in elutes in the waste before stabilization in the bioreactor with active aeration

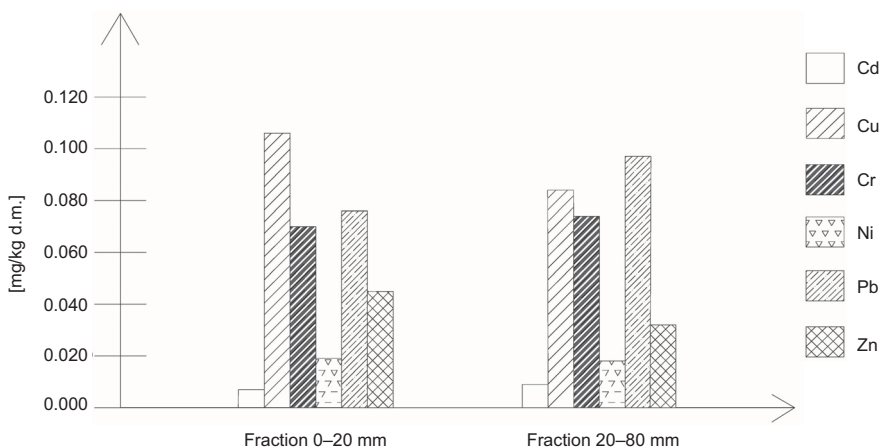


Fig. 5. Heavy metals analysis in elutes in the waste after 7-day stabilization in the bioreactor with active aeration

Conclusions

The 7-days biodrying processes were completed with decreased 10.61 % of moisture content in the 20–80 mm fraction, and 14.52 % decrease in the 0–20 mm fraction. The amounts of chlorides, identified in water extract, increased 1.5 times in stabilized waste. However, the amount of Cl^- is lower than limit values of 15 000 mg/kg of dry matter determined by Decree of the Minister of Economy [4]. There is a noticeable dominance 7 614.69 mg/kg d.m. of SO_4^{2-} anions in the water extract fraction 0–20 mm, but it is still below the acceptable level of 20 000 mg/kg d.m. defined in law regulation [4].

Decomposition of complex substances into simpler and partly mineralized matter are results of stabilization processes [14]. Therefore, the amount of heavy metals in stabilat fractions was decreased. The largest increase, up more than 75 %, was observed

in the case of chromium. As a result of the changes taking place in the stabilat, a significant increase in the content of copper was detected, that amounted to 69.55 % for the 0–20 mm fraction and 61.44 % for the 20–80 mm fraction. The smallest average increase of 10.82 % was observed for nickel. The metal content in the waste is conditioned by the presence of unwanted materials for example: ferrous and non-ferrous metals and hazardous waste such as batteries, fluorescent lamps. Segregation of waste „at the source” is needed solution to reduce the content of heavy metals in the waste directed to biological treatment [15].

The amount of heavy metals is in the limit of detection. Limited values in accordance with annex 3 [4] are in [mg/kg d.m.]: Cd = 1, Cu = 50, Cr = 10, Ni = 10, Pb, and Zn = 10 = 50.

Loss on ignition of raw waste was 62.10 % d.m. After stabilization LOI was much lower (24.80 % d.m for 0–20 stabilat fraction and 49.20 % d.m. for 20–80 mm fraction). According to requirements for MBS technology [5] LOI should be lower than 35 %. Therefore, only the fraction of 0–20 mm had been properly treated in MBS technology.

In accordance with the criteria in the Regulation [4], none of the stabilized fraction can't be landfilled. Losses on ignition are much higher than the limit value of 8 % d.m. In conclusion, to fulfill the criteria set out in polish legislation [4] and [12], the biodrying process of MSW in the industrial reactor, should be extended to the point where the fraction directed to the landfill (0–20 mm) will reach LOI values lower than 8 % d.m.

The maximum 10 mgO₂/g d.m. respiration activity is the another criteria for MBS technology what was compared with results presented in Table 2. The 0–80 mm fraction was the most biologically active. The total oxygen consumption for 4-days of 0–20 mm fraction was 8.17 mgO₂/g d.m. It allows to make the conclusion that the investigated 0–20 mm fraction had been properly treated in the MBS because the respirometer activity was < 10 mgO₂/g d.m. [5].

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BADANIA BIOSUSZENIA ODPADÓW KOMUNALNYCH

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Abstrakt: Artykuł prezentuje analizę pracy reaktora służącego do mechaniczno-biologicznej stabilizacji odpadów. Odpady komunalne poddawane są wstępnej mechanicznej przeróbce, a następnie frakcja 0–80 mm najbogatsza w materię organiczną poddawana jest obróbce tlenowej w reaktorze. Przeprowadzono badania odpadów komunalnych kierowanych do reaktora (0–80 mm), a także stabilizatu (0–20 mm, 20–80 mm) powstałego po 7-dniowym suszeniu. Wyznaczono następujące parametry: straty prażenia (LOI), wilgotność, pH, siarczany, chlorki, metale ciężkie oraz aktywność oddechową. W celu określenia stabilizacji materiału mierzono ubytek O₂ i produkcję CO₂. Uzyskane wyniki pozwoliły ocenić efektywność pracy reaktora zgodnie z kryteriami prawnymi. Badania prowadzono z użyciem urządzeń zakupionych ze środków unijnych: respirometr OXYMAX ER-10, chromatograf jonowy 883 Basic IC plus, spektrometr z plazmą ICP.

Słowa kluczowe: mechaniczno-biologiczna stabilizacja odpadów, biosuszenie odpadów komunalnych, respirometria

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- CFD – computational fluid dynamics (4–5) 453, 42; (4–5) 461, 43
- ¹³C NMR – nuclear magnetic resonance spectroscopy to carbon (2) 193, 20
- COD – chemical oxygen demand (2) 271, 27
- HPLC – high-performance liquid chromatography (2) 193, 20; (2) 225, 23
- ITS – integrated trophic state index (11) 1275, 115
- LC/MS – liquid chromatography – mass spectrometry (9) 935, 86
- LNAPL – lighter-than-water non-aqueous phase liquids (1) 63, 7; (7–8) 771, 70
- MSW – municipal solid waste (12) 1461, 132
- NO₂ – nitrogen dioxide (3) 415, 40
- PAHs – polycyclic aromatic hydrocarbons (2) 225, 23; (3) 339, 33; (10) 1153, 105
- PAPR – partially acidulated phosphate rocks (12) 1451, 131
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Varia

INVITATION FOR ECOpole '14 CONFERENCE



CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 23rd annual Central European Conference ECOpole '14, which will be held in 15–18.10.2014 (Wednesday–Saturday) in Hotel Ziemowit in Jarnoltówek, PL.

The Conference Programme includes oral presentations and posters and will be divided into four sections:

- **SI Chemical Pollution of Natural Environment and Its Monitoring**
- **SII Environment Friendly Production and Use of Energy**
- **SIII Forum of Young Scientists and Environmental Education in Chemistry**
- **SIV Impact of Environment Pollution on Food and Human Health**

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format),
- extended Abstracts (6–8 pages) in the semi-annual journal *Proceedings of ECOpole*,
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

The deadline for sending the Abstracts is **15th July 2014** and for the Extended Abstracts: **1st October 2014**. The actualized list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from **31st July 2014**) on the Conference website:

ecopole.uni.opole.pl

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain abstracts of the Conference contributions as well as the Conference Programme recorded on electronic media (the Programme will be also published on the Conference website).

After the ECOpole '14 Conference it will be possible to publish electronic version of presented contributions (oral presentations as well as posters) on this site.

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**ZAPRASZAMY DO UDZIAŁU
W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI ECOpole '14
W DNIACH 15–18 X 2014 r.**



**SUBSTANCJE CHEMICZNE
W ŚRODOWISKU PRZYRODNICZYM**

Będzie to **dwudziesta trzecia z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotyczącym różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w Hotelu Ziemowit w Jarnołtówku.

Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady konferencji ECOpole '14 będą zgrupowane w czterech Sekcjach:

- **Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring**
- **SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie**
- **SIII Forum Młodych (FM) i Edukacja prośrodowiskowa**
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Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie,
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- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna (Ecol. Chem. Eng.)* ser. A i S oraz w półroczniku *Chemistry – Didactics – Ecology – Metrology (Chemia – Dydaktyka – Ekologia – Metrologia)*.

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Streszczenia oraz program konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także zamieszczony na stronie internetowej konferencji:

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Prof. dr hab. inż. Maria Waclawek
Przewodnicząca Komitetu Organizacyjnego
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- [1] Lowe DF, Oubre CL, Ward CH. Surfactants and cosolvents for NAPL remediation. A technology practices manual. Boca Raton: Lewis Publishers; 1999.
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- [7] Kowalski P. Statistical calibration of model solution of analytes. Ecol Chem Eng A. Forthcoming 2015.

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