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## COMPARISON OF THE SEQUENTIAL EXTRACTION METHODS FOR SOIL SUBJECTED TO THE LONG-TERM EFFECT OF SEWAGE

### PORÓWNANIE METOD EKSTRAKCJI SEKWENCYJNEJ GLEBY PODDANEJ WIELOLETNIEMU DZIAŁANIU ŚCIEKÓW

**Abstract:** The collation and comparison of two sequential extraction procedures: 5-stage Tessier's and less-known 4-stage Sposito's for samples of soil treated with wastewaters from the low-tonnage vegetable and animals fats production were presented. The subject production of technological fats was carried out in a small oleochemical plant and the presented results are the continuation of the previous papers. The doses of wastewaters directed to fields used for testing were limited by total nitrogen concentration in the total batches not exceeding the threshold value of 170 kgN/ha · year. The experimental plots were sown in the consecutive years with vegetation such as: oat, rape, triticale and mustard, which were introduced to the examined soils in bulk in a form of a green fertilizer. In order to compare the changes taking place in time, the acreage of the fields used for testing was fertilized with the separately mixed raw wastewaters after their defatting and physicochemical pretreatment. Fertilization processes were carried out on regular basis once a year within the period of four years. The soil samples used for the analyses were taken from the surface layer from the experimental fields. The obtained results indicate the significant variability of changeability levels concerning exchangeable and residual fractions determined in accordance with the selected sequential extraction methods.

**Keywords:** sequential extraction procedures, wastewaters from oleochemical production, exchangeable fractions, residual fractions

#### Introduction

Pretreated industrial wastewaters from the production of industrial fats of vegetable and/or animal origin produced in small oleochemical plants have the beneficial N:P:K ratio for the fertilization needs [1]. The essential condition for the agricultural use of such wastewaters is their effective defatting and the elimination of colloidal and suspension systems [2, 3]. In specialist literature, there are some examples of papers concerning the issue of agricultural utilization of wastewaters from the production of vegetable or animal fats production including the aspect of total changes in heavy metal concentrations being the result of agricultural utilization [4-10]. However, there have been only few reports on changeability of the individual fraction fields observed during many years of carrying out experiments concerning soil fertilization with such wastewaters. This issue seems to be particularly essential because the total metals concentrations do not reflect the changes taking place with their participation and the participation of wastewaters pollutants' load components during many years of providing the soil with these substances.

The aim of the paper was the quantitative identification of the dynamics of fractional changeability taking place in the surface layer of soil in case of two fractions: the exchangeable one and the residual one for the selected heavy metals during the period of

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four-year agricultural utilization of defatted raw and physicochemically pretreated wastewaters from the low tonnage oleochemical production. In order to achieve this aim, one of the frequently used for soil assessment sequential extraction methods, that is the 5-stage Tessier's procedure [11] and the less known 4-stage Sposito's procedure [12] were applied.

## Materials and methods

### *Study area and soil sampling*

Soil from the experimental fields was rated as the light soils category with sandy granulometric composition - sandy clay loam in plough and decayed material layer. The examined soils were produced from glacial till and they have the genetic material sequences typical of the category of brown soil, soil profile: Ap-Bw-Ck [13]. Before the experiment, the soil reaction was acidic, pH in 1.0 M KCl  $3.7 \pm 0.2$  and the active acidity (in distilled H<sub>2</sub>O) measured potentiometrically was pH  $6.7 \pm 0.2$ . The average decay content in the accumulation layers was 13.21 g/kg and the organic carbon 7.66 g/kg, and the total nitrogen content was 0.70 g/kg, plant assimilable forms of phosphorus amounted 52.0 mg P<sub>2</sub>O<sub>5</sub>/kg, potassium 27.0 mg K<sub>2</sub>O/kg and magnesium - 14.0 mg/kg.

Doses of wastewaters directed to fields used for testing were limited with total nitrogen concentration, in portions not exceeding the amount of 170 kg N/ha·year. The experimental plots were sown every year in the consecutive years with vegetation such as: oat, rape, triticale and mustard, which were introduced to the examined soils in bulk in a form of green fertilizer. Soil samples from the fields used for testing (50.0 acres each) fertilized with mixed defatted raw wastewaters and the pretreated ones were taken in accordance with the Polish standard PN-ISO 10381-2 from the surface layer 0.0-20.0 cm. The soil reaction sample was determined in accordance with the methods given in PN-ISO 10390:1997. The soil material for the analyses of the total heavy metals contents was taken within 4 years in equal monthly intervals.

### *Soil analysis*

Soil samples collected from the areas of experimental plots were sequentially extracted acc. to Sposito's and Tessier's methods [11, 12], by using air dried analytical samples (40.0 g each) which were treated with extracting solutions of increasing extraction power (Table 1).

After filtering solid parts, the filtrate was analyzed by using AAS (apparatus: BUCK Scientific 210 VGP and Spectr AA Varian 220 SS). The soil specimens, washed with water and dried, were used at the next stage of the extraction - at I (Tessier and Sposito), IV (Sposito) and V (Tessier) fractions. The results of the filtrate analyses for the contents of Cd and Zn in first and fifth (fourth) speciation fractions during four experimental years are presented in Figures 1 and 2.

Table 1

Sposito's and Tessier's procedures used for fractionation analysis

No	Fraction	Extraction steps <sup>a)</sup>
Sposito's procedure [12, 14, 15]		
1	I Exchangeable	a-1) 400 cm <sup>3</sup> 0.5 M KNO <sub>3</sub> , shaken at 25°C (16.0 h).
	II Sorbed	a-1.1) 400 cm <sup>3</sup> deionized water, shaken at 25°C (2.0 h).
	III Organic	b-1) 400 cm <sup>3</sup> 0.5 M NaOH, shaken at 25°C (16.0 h).
	IV Carbonate and sulfide forms	c-1) 400 cm <sup>3</sup> 0.05 M Na <sub>2</sub> EDTA, shaken at 25°C (6.0 h). d-1) 400 cm <sup>3</sup> 4.0 M HNO <sub>3</sub> , shaken at 80°C (16.0 h).
Tessier's procedure [11, 14-16]		
2	I Exchangeable	a-2) 320 cm <sup>3</sup> 1.0 M CaCl <sub>2</sub> (pH 7), shaken at room temperature (1.0 h).
	II Carbonate	b-2) 320 cm <sup>3</sup> 1.0 M CH <sub>3</sub> COONH <sub>4</sub> acidifying with 80% CH <sub>3</sub> COOH up to pH 7 and shaken at room temperature (5.0 h).
	III Bound to Fe and Mn oxides	c-2) 800 cm <sup>3</sup> 0.04 M NH <sub>2</sub> OH·HCl in 25% CH <sub>3</sub> COOH (pH 2) shaken at 96 ± 3°C (5.0 h).
	IV Organic	d-2) 120 cm <sup>3</sup> 0.02 M HNO <sub>3</sub> and 200 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> (pH 2) shaken at 85 ± 2°C (3.0 h). d-2.1) 200 cm <sup>3</sup> 3.0 M CH <sub>3</sub> COONH <sub>4</sub> in 20% HNO <sub>3</sub> (v/v) was added and shaken at room temperature (pH 2) (0.5 h).
	V Residual	e-2) 120 cm <sup>3</sup> HNO <sub>3</sub> and 200 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> were added and mixed (pH 2). The mixture was shaken at boiling point and at that time it was treated twice with HNO <sub>3</sub> and H <sub>2</sub> O <sub>2</sub> up to the moment of releasing white fumes (1.0 h). 200 cm <sup>3</sup> 30% H <sub>2</sub> O <sub>2</sub> was added and was shaken at boiling point (0.5 h).

<sup>a)</sup> sequential extractions were carried out using 40.0 g dried at room temperature soil samples

### *Physicochemical method for pretreatment of wastewaters from the oleochemical production*

The simplified technological scheme of physicochemical installation in the wastewaters treatment plant where the pretreatment of mixed wastewaters from the subject oleochemical production was carried out was presented with the detailed description in paper [1]. Post production wastewaters from the production of fats of vegetable and animals origin were directed to the preliminary chamber to be mixed and averaged and then pumped into the aerated chamber at the first stage of pretreatment where hydrogen peroxide was additionally introduced in doses 150.0-175.0 g H<sub>2</sub>O<sub>2</sub>/m<sup>3</sup> of wastewaters in order to separate the protein and fat flotote. Pretreatment at the second, chemical stage was carried out with lime milk (in unit doses 1.25-1.50 kg CaO/m<sup>3</sup> of the defatted wastewaters after the first stage of pretreatment) with the final flocculation with aqueous 0.3% flocculant solution (Praestol 859 BC Stockhausen dosed in the amount of pure component 50.0 g/m<sup>3</sup> of wastewaters). The process was additionally aided with dissolved air flotation (DAF) (basic flotation parameters: saturation time 10.0 min, saturation pressure 500 kPa, the level of pretreated wastewaters recirculation 20%) and oxidized with hydrogen peroxide in doses 235.0-250.0 g H<sub>2</sub>O<sub>2</sub>/m<sup>3</sup> of wastewaters. After oxidation and separation of phases, the flotote was directed to the tank to be additionally condensed and next to the plate and frame filter press in order to be dehydrated, while the pretreated wastewaters were directed to the storage tank from where they were directed to experimental fields.

## Results and discussion

The subject production of technological fats of vegetable and animal origin was carried out in a small oleochemical plant located in the rural area, and the presented results of the research are the continuation of papers [1, 2]. The aim of this study was the quantitative identification and the comparison of the dynamics of changes in two fractions, that is the exchangeable one and the residual one, obtained after the application of Tessier's extraction procedures (fractions I and V) and Sposito's extraction procedures (fractions I and IV) for such heavy metals as Cd and Zn. The dynamics of changes was analyzed in the surface soil layer (0.0-20.0 cm) during the period of four-year agricultural utilization of the defatted raw and physico-chemically pretreated, mixed wastewaters from the subject production. In order to compare the changes taking place over time, the acreage of the experimental fields was fertilized with the separately mixed raw wastewaters after their defatting and with the ones which were physico-chemically pretreated. During the experimental period, the ranges of basic parameters values for the mixed raw wastewaters after their defatting and the ones which were physico-chemically pretreated were in accordance with the data given in Table 2.

Table 2  
Compilation of ranges of basic parameters values for the raw and physico-chemically pretreated wastewaters directed to the experimental plots [1, 2]

Item	Parameter	Unit	Crude wastewater	Pretreated wastewater <sup>a)</sup>
1	Reaction (pH)	[-]	3.9-5.0	8.4-9.3
2	Total suspended solids (TSS)	[mg/dm <sup>3</sup> ]	477.3-2530.0	18.9-42.7
3	Chemical oxygen demand (COD <sub>r</sub> ) <sup>b)</sup>	[mg O <sub>2</sub> /dm <sup>3</sup> ]	3348.9-10201.6	809.6-4405.7 <sup>b)</sup>
4	Biochemical oxygen demand (BOD <sub>5</sub> )	[mg O <sub>2</sub> /dm <sup>3</sup> ]	905.8-4593.9	467.9-2067.8
5	Total nitrogen (TN)	[mg N/dm <sup>3</sup> ]	175.3-720.9	88.8-170.7
6	Total phosphorus (TP)	[mg P/dm <sup>3</sup> ]	60.7-220.8	11.3-40.8
7	Ether extract (EE)	[mg/dm <sup>3</sup> ]	703.3-5999.0	3.7-27.3
8	Potassium (K)	[mg/dm <sup>3</sup> ]	149.4-606.2	66.9-483.7

<sup>a)</sup> range of values after two stages of pretreatment; <sup>b)</sup> using H<sub>2</sub>O<sub>2</sub>, the values of COD were given as corrected ones: COD<sub>r</sub> = COD<sub>p</sub> - f·c (f = 0.25 based on the data from the study [17, 18])

In case of soil samples being subject to raw defatted wastewaters, their acidity over time was found from the initial level of pH<sub>0</sub> ≈ 6.7 ± 0.3 to the final value pH<sub>K</sub> ≈ 5.9 ± 0.4 (there was no liming of this experimental plot, and the raw wastewaters after the defatting process have the reaction pH ≈ 3.9-5.0). In soil samples, where pretreated wastewaters with reaction pH = 7.8-8.8 were applied during the four years of experiments, no significant change of this parameter was found because its level was within pH ≈ 6.7 ± 0.2, during the whole experimental period. On the basis of the carried out analyses of the soil samples it was found that cadmium and zinc concentrations remained at the level of natural background in case of the subject soils. There was no significant influence of dosing wastewaters on the level of the registered values of these metals. The total load did not undergo any changes during the experimental period and was roughly in accordance with the polynomial equation  $C_M(t) = at^2 + bt + c$  (where:  $C_M$  - total Cd or Zn concentration determined with the use of AAS, and parameter  $t$  means experimental time expressed in monthly units) [2].

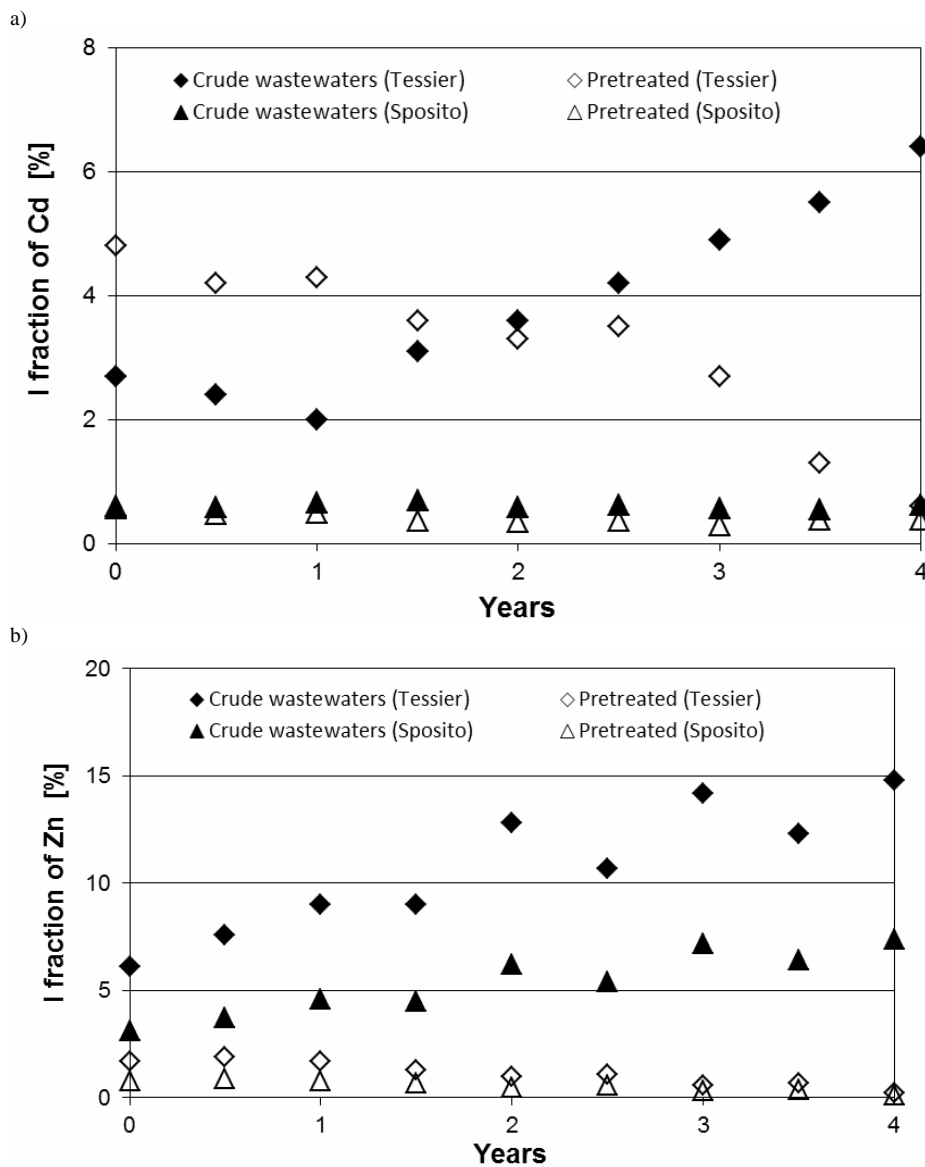


Fig. 1. Comparison of changes in exchangeable fraction contents (fraction I) for: a) cadmium and b) zinc within the period of four-year fertilization with raw defatted wastewaters and the ones which were physico-chemically pretreated and originated from oleochemical production

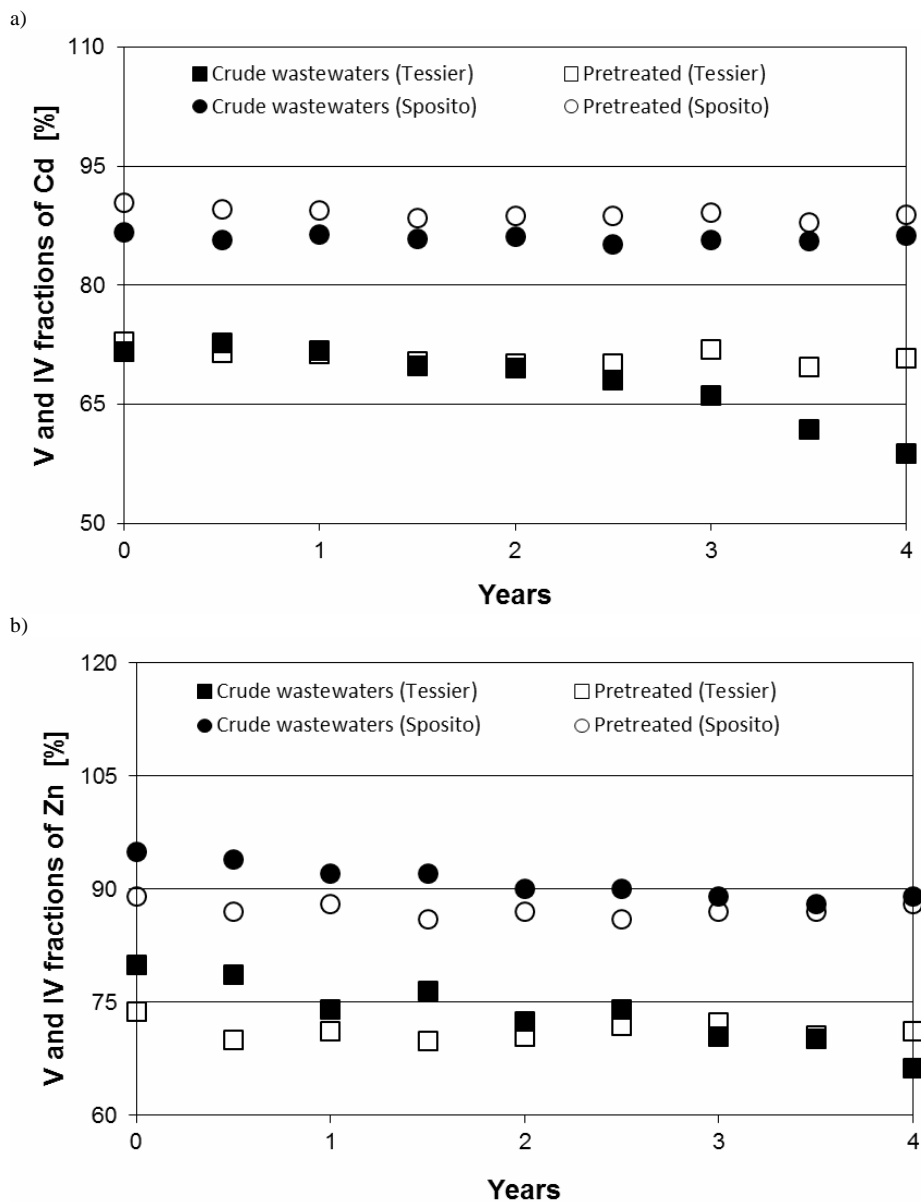


Fig. 2. Comparison of changes in the residuals fraction (fraction IV in Sposito's procedure and fraction V in Tessier's procedure (Table 1)) for: a) cadmium and b) zinc within the period of four-year fertilization with raw defatted wastewaters and the ones which were physico-chemically pretreated and originated from oleochemical production

Cadmium concentrations registered during the experimental period did not exceed the level of 1.0 mg/kg dry mass and they were around the values of 0.6 ( $\pm 0.2$ ) mg/kg dry mass. The zinc contents in the determined samples respectively fluctuated around  $49.7 \pm 2.7$  mg/kg dry mass, not exceeding the values for such type of soils applied to agricultural utilization [3]. In case of fraction I determined for cadmium and zinc, the results obtained with the use of Tessier's and Sposito's extraction procedures differed both with regard to results obtained for soil samples treated with raw, defatted as well as physico-chemically pretreated wastewaters (Fig. 1a and b).

In case of cadmium, the higher percentage content of leachable fraction determined with Tessier's method was obtained with the increasing trend in its quantity in line with the time of long-term dosing of raw defatted wastewaters. However, in case of Sposito's procedure, no evident tendencies or trends were registered over the time of dosing during the whole experimental period (Fig. 1a). In case of this fraction's content, determined in soils treated with physico-chemically pretreated wastewaters, the application of Tessier's procedure allowed to determine the content with the evident tendency of its successive decrease over time and the stable level in case of content determined in accordance with Sposito's procedure (Fig. 1a). In case of zinc, the determined contents of fraction I for soil samples treated with raw defatted wastewaters differed in values - the ones obtained in accordance with Tessier's procedure contained higher levels of values (from 6 to 14.9%) than the ones received with the use of Sposito's procedure (from 3 to 7%) (Fig. 1b). In case of contents analyses of this fraction for the soil samples treated with physico-chemically pretreated wastewaters equal stable values were obtained in the experimental period (Fig. 1b). Therefore, the thesis can be suggested that in case of soil being subject to long-term treatment with raw defatted wastewaters but without lime there are transformations leading to the increase in cadmium ion-exchange resin. This parameter functionally depends on a range of factors including the reaction value concerning the soil environment [19-22]. The labile forms of metal fractions which are present in soils significantly influence Cd and Zn mobility, bioaccessibility and toxicity [15]. Definitely, the highest percentage participation was registered in case of so called residual fraction (fraction V in Tessier's method and fraction IV in Sposito's procedure). In case of soil samples treated with pretreated wastewaters, cadmium and zinc contents in this fraction were registered at the level around 70% (Tessier's method) and above 85% (Sposito's method). In case of fraction V, being the residual load for soil samples treated with defatted raw wastewaters, the decrease in the qualitative content registered over time was observed in case of any metal (Fig. 2a and b). The lowest one was in case of zinc - around 10-15%. The residual fraction is the load which is the least determined with regard to its qualitative and structural content and its properties significantly depend on local soil formation and environmental conditions, which at the same time makes it difficult to describe and interpret it fully and only on the basis of quantitative changes taking place over time [1, 19, 23].

## Conclusions

Analyzing the fractional content with the use of two extraction procedures during the experimental period, different percentage levels of the determined fractions are obtained

and often the different trends during the time of long-term treatment of the examined soils with wastewaters. On the basis of the comparison of results obtained for an exchangeable fraction and the so called residual fraction, it is difficult to explicitly characterize the direction of changes taking place between the fraction loads in soils being subject to long-term treatment with wastewaters from oleochemical production. In case of cadmium, the phenomenon of significant differences in percentage participation of fractional loads over time should be also assessed with regard to random scattering of the received values, considering its relatively low concentration in soil (for  $Cd_{(0)} = 0.6 (\pm 0.2)$  mg/kg dry mass), and at the same time the statistical assessment of the obtained results.

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## **PORÓWNANIE METOD EKSTRAKCJI SEKWENCYJNEJ GLEBY PODDANEJ WIELOLETNIEMU DZIAŁANIU ŚCIEKÓW**

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w Bydgoszczy

**Abstrakt:** Przedstawiono zestawienie i porównanie dwóch procedur ekstrakcji sekwencyjnej: 5-etapową Tessiera oraz mniej znaną 4-etapową Sposito dla próbek gleby traktowanej ściekami z małonażowej produkcji tłuszczów roślinnych i zwierzęcych. Przedmiotowa produkcja technicznych tłuszczów była prowadzona przez mały zakład oleochemiczny, a prezentowane wyniki są kontynuacją dotychczasowych prac. Dawki ścieków kierowanych na poletkę doświadczalną limitowano stężeniem azotu ogółem w łącznych porcjach nieprzekraczających granicznej ilości 170 kg N/ha-rok. Poletkę testowe corocznie były obsiewane roślinnością, w kolejnych latach: owsem, rzepakiem, pszenżytem i gorczycą, które w formie zielonego nawozu były w całej masie wprowadzane do badanych gleb. Dla porównania zachodzących zmian w czasie, eksperymentalne arealty nawożono oddzielnie mieszanyimi ściekami surowymi po ich odtłuszczeniu i podczyszczonymi fizykochemicznie. Nawożenie prowadzono regularnie raz w roku w okresie czterech lat. Próbkę gleby do analiz pobierano z powierzchniowej warstwy z poletek doświadczalnych. Uzyskane wyniki wskazują na znaczące zróżnicowanie poziomów zmienności frakcji jonowymiennych i pozostałych oznaczanych zgodnie z wytypowanymi metodykami ekstrakcji sekwencyjnej.

**Słowa kluczowe:** procedury ekstrakcji sekwencyjnej, ścieki z produkcji oleochemicznej, frakcje wymienna oraz pozostałość