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ANALYSIS OF PHOSPHORUS SPECIATION IN PRIMARY SLUDGE IN THE ANNUAL CYCLE

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Abstract. The objective of the research was to investigate phosphorus speciation in sewage sludge in order to determine the amount of the element that can be assimilated by plants after the application of sludge for nature-related purposes. Since the possibility of using sludge for such purposes is of considerable importance, this paper analyses the content of different phosphorus speciation forms (including the bioavailable ones) in primary sludge. The studies' results indicate that the maximum share of mobile forms (Ca-EDTA+Na-EDTA) in primary sludge in the annual cycle amounts to merely 46 %. This confirms the observation that in the examined period the hardly-available, organic phosphorus forms are dominant (fractions H_2SO_4 and NaOH). Therefore, after the application of primary sludge for nature-related purposes, only a small portion of phosphorus included therein is assimilated by plants.

Key words: primary sludge, phosphorus speciation, application of primary sludge for nature-related purposes.

1. Introduction

Phosphorus is a key and indispensable element, necessary for the proper functioning of organisms. It is an ingredient of i.a. adenosine triphosphate molecules, which play a fundamental role in the transfer and storage of energy in every living organism. The presence of phosphorus in the early stages of the plant's growth provides the appropriate root formation and, consequently, its resistance to drought and nutrient deficiency in later stage of development [1]. On the other hand, the excess of this element in the aquatic environment contributes to water eutrophication. Therefore, it is extremely important to maintain a rational management of this element.

The depletion of natural deposits of phosphorus – the most important material for the manufacturing of fertilizers – means that alternative sources of this element should be sought. Sewage sludge containing phosphorus, nitrogen, calcium, magnesium and potassium provides valuable feedstock for phosphorus fertilizers. The studies on phosphorus speciation fulfill the need to determine the possibilities of obtaining phosphorus from sewage sludge.

In 1970s the term *speciation* was incorporated into environmental chemistry. The explanation of this term is best defined by the statement: *The speciation describes the physical and chemical forms of the element found in a given environmental matrix* [2].

Functional speciation describing the element's division into forms with specific chemical and biological activities is one of speciation types. The examination of this type of sludge speciation allows determining the amount of phosphorus that can be assimilated by plants after sludge application for nature-related purposes. The possibility of sludge application for such purposes is very important, therefore this paper analyzes the shares of different speciation forms (including bioavailable ones) of phosphorus in primary sludge.

2. Methodology of research

The studies examined sludge collected at two wastewater treatment plants: A and B, both of which use a primary clarifier in the technological process. The content of different phosphorus fractions was determined in three series of sludge sampling using the fractionation scheme proposed by Golterman [4]. This procedure is characterized by the lack of interaction between extraction reagents and the calcium carbonate present in the sludge, the unobstructed access of the subsequent extractant to the sludge, and the relatively short duration of analysis. The first step involved a 4-hour extraction with Ca-EDTA solution. In the second stage, the samples were extracted for 18 hours with

Na-EDTA solution. The next step consisted in the 2-hour extraction of the sample with a solution of H_2SO_4. The final stage, which also lasted 2 hours, involved the use of NaOH solution for the extraction. After each extraction stage the samples were filtered and the post-filtration residue was treated with the subsequent extraction reagent. The total phosphorus concentration was determined in the obtained filtrate. Phosphorus determination was performed by spectrophotometric method using MARCEL MEDIA UV-VIS spectrophotometer. The measurement was conducted according to the orthophosphate determination procedure using phosphate-molybdenum blue and the total phosphorus determination following the sample oxidation with potassium peroxodisulphate (VI) [5].

Table 1

Phosphorus sequential extraction scheme according to Golterman [4, 12]

Stage	The extraction conditions	Fraction
1	0.05 M Ca-EDTA (twice extraction), 2h	phosphorus associated with oxides and hydroxy oxides of iron, aluminium and manganese
2	0.1 M Na-EDTA, 18 h	phosphorus associated with carbons
3	0.5 M H_2SO_4, 2 h	phosphorus is presented in the soluble organic matter bonds
4	2 M NaOH, 2 h	the remaining phosphorus, bonded with aluminosilicates and organic matter contained in the form of connections, which is not subject to the action of sulfuric acid in stage 3

3. Results

The primary clarifier receives wastewater devoid of large mineral particles (e.g. sand), rich in organic and colloidal substances and suspended solids. With the wastewater laminar flow rate being sufficiently low, the sedimentation of easily settleable suspended solids, whose density is slightly higher than water's, is possible in the primary clarifier. The composition of the wastewater reaching the primary clarifier nay depend on the extent of decay, the kind of suspended solids and the amount of industrial waste. Fig. 1 and 2 show the results of phosphorus speciation analysis of primary sludge collected at the two wastewater treatment plants. These results indicate a large variation in the value of the analyzed speciation forms in the annual cycle.

The mere analysis of the variability in the share of mobile phosphorus forms in the annual cycle (Fig. 3 and 4) also shows a significant variation in the values, which may be due to the high compositional instability of the raw sewage reaching the primary clarifier.

Further analyzes required checking the correspondence between the statistical distributions of mobile forms shares and the normal distribution and for this purpose the Shapiro-Wilk test was used to verify null hypotheses and alternative forms:

H0: the distribution of mobile forms shares is a normal distribution

H1: the distribution of mobile forms shares is not a normal distribution

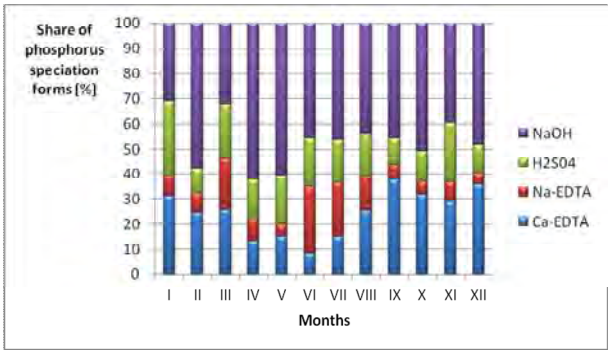

Fig. 1. Shares of different phosphorus fractions in primary sludge collected at wastewater treatment plant A

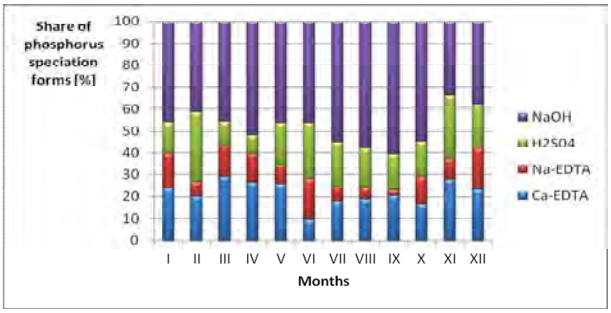

Fig. 2. Shares of different phosphorus fractions in primary sludge collected at wastewater treatment plant A

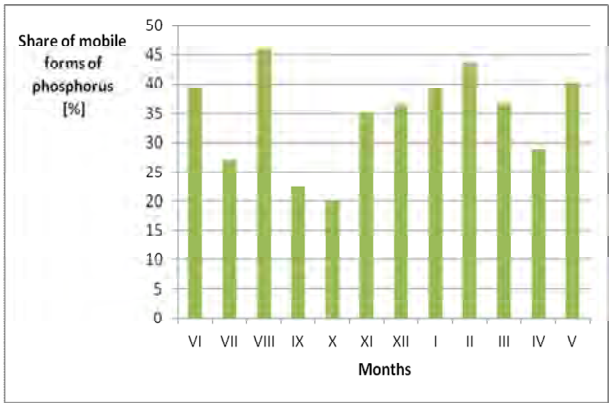

Fig. 3. Share of mobile phosphorus fractions (Ca-EDTA + Na-EDTA) in primary sludge collected at treatment plant *A*

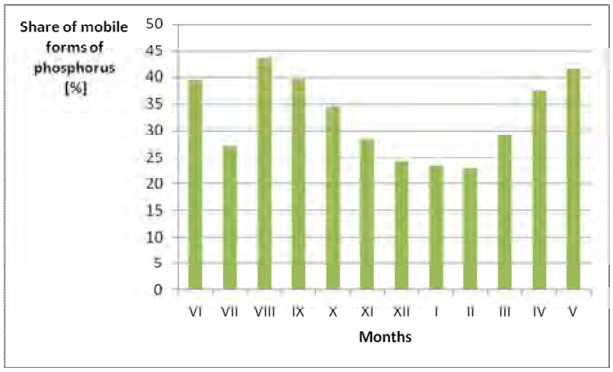

Fig. 4. Share of mobile phosphorus fractions (Ca-EDTA + Na-EDTA) in primary sludge collected at treatment plant *B*

The results of the calculations (Table 2) show that at the significance level of $\alpha = 0.05$ there is no reason to reject the hypothesis ($p > \alpha$) that the analyzed mobile forms shares for the sewage treatment plants deviate from normal and indicate that it is possible to conduct further statistical analyzes.

Table 2

Shapiro-Wilk test results (p) for the mobile forms shares for wastewater treatment plants *A* and *B*

Wastewater treatment plant	p
B	0.1234
A	0.3245

The next stage involved plotting box charts taking into account the mobile forms shares in the analysed plants in the annual cycle. The ends of the whiskers in the box charts represent minimum and maximum figures of mobile forms shares. The analysis of the box charts show that the mobile forms shares in primary sludge ranged from 20 % to 46 %.

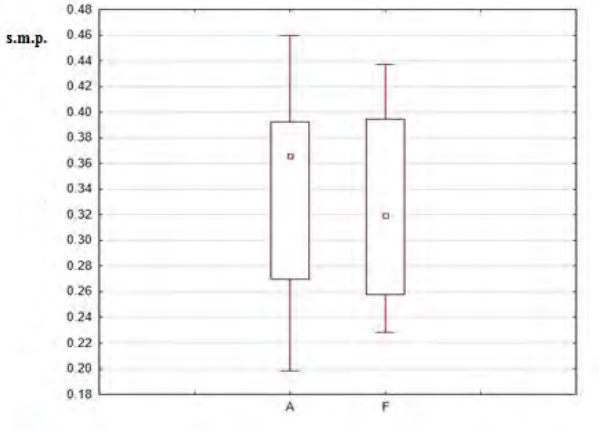

Fig. 5. Scopes of shares of mobile phosphorus (Ca-EDTA and Na-EDTA) forms (s.m.p.) in the primary sludge collected at the treatment plants *A and B*

4. Conclusions

The maximum value of the mobile forms share (Ca-EDTA + Na-EDTA) in primary sludge in the annual cycle, amounting to 46 %, confirms that hardly-accessible, organic phosphorus forms (H_2SO_4 and NaOH fractions) are dominant in primary sludge. Therefore, after the application of primary sludge for nature-related purposes, only a small portion of the phosphorus contained therein will be assimilated by the plants.

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