Abstract. The object of the study was to evaluate the effects of the phosphorus dosage and incubation time on available phosphorus forms and the content of exchangeable aluminium in Dystric Cambisols under conditions of a model laboratory experiment. Mineral phosphorus \([\text{Ca(H}_2\text{PO}_4)_2]\) was added in 5 different doses to soil, incubated for 30 or 60 days at 18°C. Soil samples were analysed for available phosphorus forms, total phosphorus and the content of exchangeable aluminium. It was found that the content of available phosphorus forms depended significantly on the phosphorus dose and the incubation time. A higher content of available phosphorus was assayed after a longer incubation time. Exchangeable aluminium occurring in the samples reduced available phosphorus concentration from 1.7 to 78.2% of the amount introduced as the fertiliser.

The content of available phosphorus forms in the soil depends on the interaction of many factors, such as soil acidity, ion activity, solubility of phosphates, the degree of weathering of the soil’s components, the amount and solubility of organic matter, fertilisation, etc. \([9, 10]\). Even if during transformations of soil those factors change, soil phosphorus forms change too \([13]\). In acid soils of pH below 5.5, the solubility of aluminium compounds rapidly increases. In consequence, the intake of nutrients, especially phosphorus, by the roots is limited. It seems that aluminium affects the solubility of phosphorus in the environment, and thus reduces the intake and the use of this component by plants \([6, 7, 16]\).

The object of this paper was to evaluate the effect of the phosphorus dose and incubation time on the retarding of available phosphorus forms and the content of exchangeable aluminium in the soil under conditions of a model laboratory experiment.

*Prof. E. Spychaj-Fabisiak, DSc., Department of Agrarian Chemistry; **Prof. J. Długosz, DSc., Department of Soil Science and Soil Protection; ***R. Zamorski, DSc.; Department of Biochemistry; University of Technology and Agriculture, 85-029 Bydgoszcz, Seminaryjna 5, Poland.
MATERIALS AND METHODS

The laboratory experiment was carried out with the use of Dystric Cambisols [17] collected from the 0-25 cm layer of a particle size typical for loamy sand [15]. The soil material was taken from a productive field at Pieczyska near Bydgoszcz. The soil was chosen mainly because of its reaction (Table 1). It was not abundant in phosphorus or potassium (as determined according to the standard Egner-Riehm method) and was strongly acidic.

The experiment was carried out in three replications with the use of airtight PCV containers 15 cm high and of 12.5 cm diameter. The containers were filled with the 1 kg soil deposit.

Prior to incubation mineral phosphorus in the form of Ca(H$_2$PO$_4$)$_2$ was added to the doses: 0, 6, 12, 18, and 24 mg P per 1 kg soil. These fertiliser doses corresponded with 0, 15, 30, 45 and 60 kg P per hectare, respectively. The soil was incubated for 30 or 60 days. The investigations proceeded under controlled conditions (temperature 18°C, moisture 60% maximum water capacity). After incubation, the soil samples were collected and analysed for available phosphorus forms, total phosphorus (according to molibdo-vanado-phosphoric acid colorimetric methods) [14] and the content of exchangeable aluminium extracted with 1 M KCl.

The results were evaluated with variation analysis for a two-factor experiment carried out as an independent series with the use of the evaluation of difference significance according to the Tukey Test at p = 0.05. The factor studied was phosphorus doses (n = 5, factor I) and incubation time (n = 2, factor II).

RESULTS AND DISCUSSION

The availability of phosphorus depends on the conditions at which it undergoes sorption as well as the magnitude of chemical and biological transformations of phosphorus in the soil [1-3, 5]. The content of phosphorus mineral fractions is related to soil acidity, liming, mineral fertilisation, especially with phosphorus. Soil acidity is crucial for inter-relations of phosphate ions (H$_2$PO$_4^-$ and HPO$_4^{2-}$) in

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>pH in KCl</th>
<th>Hydrolytic acidity mmol H$^+$ kg$^{-1}$</th>
<th>N$_{tot}$</th>
<th>C$_{org}$</th>
<th>Al Exch.</th>
<th>H</th>
<th>P</th>
<th>K</th>
<th>Al:P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pieczyska</td>
<td>4.4</td>
<td>21.9</td>
<td>0.43</td>
<td>3.18</td>
<td>1.21</td>
<td>3.79</td>
<td>48.1</td>
<td>13.5</td>
<td>0.679</td>
</tr>
</tbody>
</table>

TABLE 1. THE PHYSICO-CHEMICAL PROPERTIES OF THE SOIL
the soil solution [1]. $\text{H}_2\text{PO}_4^-$ ions prevail in acid soils, while the other ion is more abundant in alkaline soils. The concentration of available phosphorus forms in the soil deposits studied depended significantly on the phosphorus dose, the incubation time and the interactions of the two factors (Table 2).

**TABLE 2. THE CONTENT OF AVAILABLE PHOSPHORUS FORMS IN SOIL SAMPLES**

(mg per kg soil)

<table>
<thead>
<tr>
<th>Incubation time (days)</th>
<th>Phosphorus dose (mg per kg soil)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>46.13</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>56.70</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>62.85</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>62.92</td>
</tr>
<tr>
<td>30</td>
<td>55.21</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>59.22</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>57.22</td>
<td></td>
</tr>
</tbody>
</table>

Factor I (phosphorus dose) – 1.507 I x II 2.132, Factor II (incubation time) – 0.953.

After adding 12, 18 and 24 mg P per kg soil, a significant differentiation of available phosphorus forms, determined according to Egner and Riehm, was found as compared with the control and the lower dose of this element (6 mg P per kg soil).

The means calculated after 60 incubation days indicated a higher content of available phosphorus forms in comparison with those determined for soil samples after 30 days of incubation. A higher increase of the content appeared mainly in the case of the control object and at the lowest phosphorus dose used (12.9 and 13.2%, respectively). According to Borrows [4] phosphorus introduced into soil in the past not only increased its total amount - which can be desorbed- but also decreased the capacity of the soil to adsorb freshly introduced phosphates. However, Sharpley [12] stated that the amount of available phosphorus forms extractable from the soil decreases logarithmically with time.

It should be indicated here that the soil samples under study contained total phosphorus amounts ranging 0.21-0.26 g P per kg soil (mean 0.23 g P per kg soil) (Table 3).

**TABLE 3. TOTAL PHOSPHORUS CONTENT IN SOIL SAMPLES**

(mg per kg soil)

<table>
<thead>
<tr>
<th>Incubation time (days)</th>
<th>Phosphorus dose (mg per kg soil)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>0.23</td>
</tr>
<tr>
<td>30</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.23</td>
<td></td>
</tr>
</tbody>
</table>

Factor I (phosphorus dose) – 0.020 I x II N.I., Factor II (incubation time) – 0.013.
Increasing doses of super-phosphate, with the exception of the 24 mg P per kg soil, increased the percentage of available phosphorus forms in the total phosphorus (Table 4).

**TABLE 4. PERCENTAGE OF AVAILABLE PHOSPHORUS FORMS IN TOTAL PHOSPHORUS IN SOIL SAMPLES**

<table>
<thead>
<tr>
<th>Incubation time (days)</th>
<th>Phosphorus dose (mg per kg soil)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>20.0</td>
<td>22.8</td>
</tr>
<tr>
<td>60</td>
<td>20.4</td>
<td>24.5</td>
</tr>
<tr>
<td>Mean</td>
<td>20.2</td>
<td>23.7</td>
</tr>
</tbody>
</table>

The content of exchangeable aluminium in the soils under study was related to the phosphorus dose and depended on the interaction between the phosphorus dose and the incubation time (Table 5).

**TABLE 5. CONTENT OF EXCHANGEABLE ALUMINIUM IN SOIL SAMPLES (mg per kg soil)**

<table>
<thead>
<tr>
<th>Incubation time (days)</th>
<th>Phosphorus dose (mg per kg soil)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>24.60</td>
<td>21.53</td>
</tr>
<tr>
<td>60</td>
<td>26.26</td>
<td>21.77</td>
</tr>
<tr>
<td>Mean</td>
<td>25.43</td>
<td>21.65</td>
</tr>
</tbody>
</table>

Factor I – 1.112   1 x II 1.573, Factor II – n.i.

On average, the highest concentration of aluminium was found in soil of the control objects without super-phosphate. Unexpectedly comparable results were obtained both after the use of the lowest and the highest as well as the medium dose (12 and 18 mg P per kg soil). This was probably the result of the unbalanced molar ratio of calcium introduced into the soil with phosphorus fertilisers in relation to exchangeable aluminium extracted from sorption complex by calcium ions. Finally, it has been commonly accepted that aluminium ions extracted can bind available phosphorus forms at a ratio of 1:3.

Mechanisms releasing the phosphorus from phosphorus fertilisers in the soil are still under study, despite the great attention it has attracted in the agricultural literature [2, 8, 9]. Processes of transferring exchangeable phosphates to non-exchangeable are described as long-term transformations or the ageing of fertilising phosphates. Immobilisation of phosphorus is caused by adsorption – occlusion and precipitation reactions. It has been found that surfaces of Al and Fe
hydroxides have a high affinity toward phosphates in acid soils. At the beginning
of these processes, amorphic colloids of aluminium and iron phosphates appear,
which are relatively good sources of phosphorus for plants. Gradually amorphic
forms become crystal phosphates, and are therefore less soluble [16].

Ions of exchangeable aluminium retarded phosphate ions depending on the
incubation time of 30 or 60 days in amounts ranging from 1.28 mg P per kg soil to
7.21 mg P per kg soil and from 4.38 to 10.87 mg P per kg soil, respectively (Fig. 1).

Aluminium ions performed an impact on retarding phosphate ions introduced
into soils with increasing super-phosphate doses. This retarding of phosphate ions
fluctuated between 1.7 and 78.18% of the phosphorus dose used as the
Ca(H₂PO₄)₂ form (Fig. 2).

![Fig. 1. Retardation of phosphates as dependent on super-phosphate dose.](image)

![Fig. 2. Retardation of phosphates expressed as a percentage of the super-phosphate dose used.](image)
Phosphate ions introduced into the soil at the lowest super-phosphate dose underwent retardation at the highest percentage. According to Hetrick and Schwab [8] the processes affecting phosphorus concentration in the soil solution are mainly the solubility and precipitation occurring in strongly acid soils. Phosphate concentration in this solution is in equilibrium with strengite \( \text{Fe(OH)}_2\text{H}_2\text{PO}_4 \) and variscite \( \text{Al(OH)}_2\text{H}_2\text{PO}_4 \).

The content of non-exchangeable aluminium (Al nexch) strongly depended on the phosphorus dose and incubation time. Along with increasing phosphorus doses and incubation time, the amount of non-exchangeable aluminium (Al nexch) increased (Fig. 3). This form of aluminium creates insoluble compounds with phosphates.

As found by Czempińska-Kamińska [6], occluded aluminium phosphates and mineral aluminium-iron phosphates occur in small amounts. These fractions retain from 0.6 to 1.8% of the total phosphorus and from 1 to 2.3% of the available phosphorus forms.

However, in Alfisols non-occluded aluminium phosphates comprise from 13.5 to 19.6% mineral phosphorus. In acid soils, resembling the one under study, phosphates can be bound by iron and create ferric phosphates such as: \( \text{H}_3\text{Fe(PO}_4)_2 \), \( \text{FePO}_4 \) as well as humus complexes [9].

The availability of phosphorus forms to plants can be determined as the ratio of bound aluminium ions to retarded available phosphorus forms. It was found that fewer phosphates were available to plants, the higher the dose of phosphorus, along with an incubation time of 60 days (Fig. 4).

After 60 days of incubation, a widening of the bound Al to retarded P ratio from 1.5 to almost 4 was noted and after using the 18 mg P per kg soil dose, extra...
incubation time did not have any effect on this ratio. As indicated by Rabikowska and Wilk [11] phosphorus introduced into soil as a super-phosphate is transferred to various chemical compounds. The longer its contact with the soil, the more connections form. In our study we found a similar tendency, especially after the use of the highest phosphorus dose (24 mg P per kg soil). This experiment should be continued with the application of slightly acidic and acidic soils degraded under the influence of anthropogenic factors, and therefore of various aluminium content.

CONCLUSIONS

1. The content of the available phosphorus forms in soil samples under study depended significantly on the phosphorus dose and incubation time as well as the interaction of the two factors.

2. A significantly higher content of available phosphorus forms was found after 60 days of incubation in comparison with an incubation time of 30 days.

3. The content of exchangeable aluminium in the samples studied ranged 18.87 -26.97 mg Al per kg soil, which resulted in a retarding of the available phosphorus forms from 1.7 to 78.2% of the amount of phosphorus introduced as a super-phosphate.

REFERENCES

WPŁYW DAWEK FOSFORU I CZASU INKUBACJI NA PROCES UWSTECZNIANIA FOSFORU PRZYSWAJALNEGO W GLEBACH PIASZCZYSTYCH

Celem badań było określenie wpływu zróżnicowanych dawek fosforu i czasu inkubacji na zawartość przyswajalnych form fosforu i glinu wymiennego w glebie brunatnej kwaśnej w warunkach modelowego doświadczenia laboratoryjnego. Fosfor mineralny był dodawany w 5 różnych dawkach do gleby inkubowanej przez 30 lub 60 dni w temp. 18°C.

W próbkach glebowych oznaczano całkowitą zawartość fosforu, zawartość przyswajalnych form fosforu i glinu wymiennego. Stwierdzono znaczący wpływ dawki fosforu mineralnego jak i czasu mineralizacji na zawartość fosforu przyswajalnego. Wyższe zawartości fosforu przyswajalnego stwierdzano po dłuższym czasie inkubacji. Występowanie glinu wymiennego powodowało obniżenie zawartości fosforu przyswajalnego od 1,7 do 78,2 % dodanej dawki fosforu.