The aim of the present research was to estimate the long-term effect of soil management in orchards on selected physicochemical properties of humus substances isolated from Luvisols. It involved determining basic parameters of humic acids extracted from soils. Samples from topsoil were collected from apple tree orchards and arable soils in the Chełmińskie and the Krajeńskie Lake Districts. The humus substances of orchard soils showed lower condensation of aromatic rings in the molecules of humic acids, which, in turn, suggests their lower chemical maturity. Similarly, the long-term soil management in orchards decreased the resistance of humic substances to chemical oxidation. The humic acids extracted from orchard soils demonstrated a higher content of aliphatic structures.

In Poland over 289 thousand ha are covered by orchards, which accounts for 0.9% of the country’s area and, at the same time 1.52% of the total acreage of arable land. In the Kujawy and Pomorze regions, orchards cover 16.5 thousand ha. One of the most frequently used tillage systems (no-tillage) in apple-tree orchards is maintaining grass stripes between the rows of trees and herbicide fallow-land under the trees [18, 23]. The soil treatment method in orchards, which involves maintaining herbicide stripes is often the cause of its acidification [2, 8]. During long-term soil use in the orchards, one shall apply calcium fertilisers regularly, which will make it possible to maintain optimal soil pH (pH 6.2 – 6.7) [13].

Soil organic matter has been widely promoted as an indicator of soil quality, one of the components of biosphere sustainability and stability, particularly in agricultural soils. Humus substances are influenced by management practices,
especially, by fertilizers and soil tillage [21]. The content of the organic matter of soil are affected by temperature, amount of rainfall, as well as the grain size composition and the method of soil use [1, 6]. Humus composition changes under different agricultural practices. The transformations in organic substances in soils under orchard growing occur under slightly different conditions than in arable fields [17]. Maintaining an adequate amount of soil organic matter in the arable soil stabilizes soil structure and makes it more resistant to degradation, and decreases bulk density.

Under specific climate conditions each soil maintains a specific equilibrium between the humification process and the mineralization of humus compounds as well as a partial leaching of soluble organic bonds deep the soil profile [11, 14]. The equilibrium is often disturbed as a result of inadequate agrotechnical practises, fertilisation and agricultural land-improvement treatments. The optimal farming system, reasonable crop rotation, the application of FYM, green fertilisers and maintaining adequate water-air conditions are among the key factors determining the reserve of humus substances in mineral soils [10].

The properties of humus substances are soil-type-specific and they can be modified by crop rotation and the decomposition rate of post-harvest crop residue [3, 5, 6, 19]. The size and molecular weight of humus substances determine their migration rate deep the soil profile [19, 20]. The characteristics of humus substances are provided based on the research into the properties of soil extracts obtained with the selective solvents as well as the analysis of the properties of separated groups of compounds, most often humic and fulvic acids. The criterion characteristic for a complex structure of humus substances are the values of absorbance of their solutions in the range of UV and VIS radiation [7, 16].

The aim of the present paper was to evaluate the effect of soil cultivation in orchards and arable Luviosols on the properties of humic acids. A comparison was made between the results of the analysis of basic physicochemical properties of soils in orchards and arable soils of the Chełmińskie and Krajeńskie Lakelands.

MATERIALS AND METHODS

The research material was made up by soil sampled from the humus horizon of Luviosols [12], formed from glacial till. Soil was sampled in the vicinity of Kiełp (Chełmińskie Lakeland), Olszewka, Tryszczyn, Wtelno (the Krajeńskie Lakeland). Further in the paper samples were provided with the following symbols: Kiełp – apple-tree orchards (K1) and (K2) and arable fields (K3), (K4); Tryszczyn (Tr) and Wtelno (Wt) – apple-tree orchards; Olszewka (Ol), Ślesin (Sl) – arable fields as well as the symbol O-PCh for both orchards of the Chełmińskie Lakeland and O-PK for both orchards of the Krajeńskie Lakeland. Arable fields of the mesoregions were marked F-PCh and F-PK, respectively. In orchards the soil was sampled for analysis from the herbicide stripes.
The selected properties of samples were determined with commonly used methods. Bulk samples from humus horizon of Luvisols were air-dried and passed through a 2.0 mm-sieve in mesh diameter. The following were assayed in the soil samples: texture with the areometric method; hydrolytic acidity, (Kappen method); cation exchange capacity (CEC) used method with BaCl_2, pH measured in 1M KCl – potentiometrically (1:2,5 soil/solution ratio); in cylinders of the capacity of 100 cm³ there was determined the current volumetric density. In the material analysed, the following were determined: the total content of carbon (TOC) and nitrogen total content using the TOCN FORMACS TM provided by SCALAR. Statistical Analysis was conducted with the cluster analysis using Ward method [24].

For humic acids (HA) separated with the Schnitzer [22] method the following were determined:

- Optic properties in the UV-VIS range using the spectrophotometer Lambda 20 provided by Perkin-Elmer. Based on the absorbance values determined at the wavelength of 280 nm (A_{280}), 400 nm (A_{400}), 465 nm (A_{465}), 600 nm (A_{600}), 665 nm (A_{665}) the following values of the coefficients were defined:
  \[ \frac{A_{280}}{A_{465}} \] – ratio of the absorbance value at the wavelength of 280 and 465 nm,
  \[ \frac{A_{280}}{A_{665}} \] – ratio of the absorbance value at the wavelength of 280 and 665 nm,
  \[ \frac{A_{465}}{A_{665}} \] – ratio of the absorbance value at the wavelength of 465 and 665 nm,

\[ \Delta \log K = \log A_{400} - \log A_{600} . \]

- The susceptibility of humic acids to chemical oxidation: to do so, there were prepared 0.02% humic acids solutions in 0.1M NaOH, which were poured with 1.5% H_2O_2 in the 1:1 ratio. Prior to and after oxidation (after 24 h) there were made measurements of the absorbance value at the wavelength of 465 nm using the spectrophotometer Lambda 20 provided by Perkin-Elmer. There was calculated a decrease in the value of absorbance of humic acids solutions of (\Delta A_u) after the reaction, expressed in % of the initial absorbance of the comparative solution:

\[ \Delta A_u = \left[ \frac{(A_0 - A_u)}{A_0} \right] \times 100\% \]

where: A_0 – absorbance of the solution prior to oxidation, A_u – absorbance of the solution after oxidation.

**RESULTS AND DISCUSSION**

**Physicochemical properties of soils**

In the humus horizon of soils of apple-tree orchards of the Krajen'ske Lakeland there was found acidic reaction, whereas neutral reaction was recorded in the orchards of the Chelmin'ske Lakeland and arable soils of the Krajen'ske Lakeland (Table 1). A slightly acidic reaction was recorded in arable soils of the Chelmin'ske Lakeland.
Lakeland. Lower contents of organic carbon (TOC) and soil organic matter (SOM) were noted both in the soils of orchards and arable fields of the Chelmińskie Lakeland, as compared with the soils of the Krajeńskie Lakeland. In soils in orchards of that mesoregion TOC ranged from 11.51 to 14.56 g kg$^{-1}$. The content of nitrogen (Nt) varied across the soils. The lowest Nt content and the lowest C/N ratio were found in arable soils of the Chelmińskie Lakeland. In the soils of the Krajeńskie Lakeland, irrespective of their method of use there was found similar values of the cation exchange capacity (CEC), which were lower than in the soils of the Chelmińskie Lakeland. The volumetric density was similar in the soils of both mesoregions and it ranged from 1.54 to 1.61 Mg m$^{-3}$. The Krajeńskie Lakeland soils demonstrated the texture of sandy loam, while in the Chelmińskie Lakeland soils there was identified fine sandy loam and sandy loam. The lowest content of clay fraction was reported in arable soils of the Krajeńskie Lakeland.

Spectrometric properties of humic acids in the UV – VIS range

The research made using the spectroscopic methods provide information on the qualitative composition (chemical composition) as well as the quantitative composition of the substance analysed. Changes in the optic density of solutions of humic acids (HAs) are presented in Table 2. The values of the coefficients of absorbance and the value Δlog K are given in Table 3.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Wt</th>
<th>Tr</th>
<th>Ol</th>
<th>S1</th>
<th>K1</th>
<th>K2</th>
<th>K3</th>
<th>K4</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH$_{KCl}$</td>
<td>5.13</td>
<td>5.23</td>
<td>7.15</td>
<td>6.91</td>
<td>6.55</td>
<td>6.86</td>
<td>5.77</td>
<td>5.72</td>
</tr>
<tr>
<td>TOC (g kg$^{-1}$)</td>
<td>13.90</td>
<td>14.56</td>
<td>11.51</td>
<td>9.68</td>
<td>7.30</td>
<td>7.60</td>
<td>8.41</td>
<td>6.64</td>
</tr>
<tr>
<td>Nt (g kg$^{-1}$)</td>
<td>1.21</td>
<td>1.38</td>
<td>1.10</td>
<td>0.93</td>
<td>0.81</td>
<td>0.85</td>
<td>0.96</td>
<td>0.75</td>
</tr>
<tr>
<td>SOM (g kg$^{-1}$)</td>
<td>23.96</td>
<td>25.10</td>
<td>19.84</td>
<td>16.69</td>
<td>12.58</td>
<td>13.10</td>
<td>14.50</td>
<td>11.45</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>11.49</td>
<td>10.55</td>
<td>10.46</td>
<td>10.41</td>
<td>9.01</td>
<td>8.94</td>
<td>8.76</td>
<td>8.85</td>
</tr>
<tr>
<td>CEC</td>
<td>11.51</td>
<td>11.25</td>
<td>19.56</td>
<td>15.83</td>
<td>8.90</td>
<td>10.11</td>
<td>9.25</td>
<td>9.46</td>
</tr>
<tr>
<td>$\rho_{o}$ (Mg m$^{-3}$)</td>
<td>1.56</td>
<td>1.59</td>
<td>1.61</td>
<td>1.54</td>
<td>1.60</td>
<td>1.59</td>
<td>1.60</td>
<td>1.59</td>
</tr>
</tbody>
</table>

TOC – total organic carbon, Nt – nitrogen total content, SOM – soil organic matter, CEC – cation exchangeable capacity, $\rho_{o}$ – actual bulk density, Orchards: Wt, Tr, K1, K2; Cultivated fields: Ol, S1, K3, K4.
It is assumed that absorbance at the wavelength of 280 nm determines the content of lignin-type compounds \[7, 16\]. Higher absorbance values at the wavelength of 280 nm were shown for humic acids isolated from arable soils of the Chelmińskie Lakeland (K3 and K4), as compared with the soils in orchard (K1, K2), although they were identified with a low content of organic carbon and total nitrogen. In the soils of the Krajeńskie Lakeland there was found no varied content of lignin-type compounds depending on the method of use. Absorbance at the wavelength of 465 nm defines the content of humus compounds at the initial stage of their decomposition. It was shown that arable soils showed a higher content of those compounds, especially on the Chelmińskie Lakeland. Based on the literature
data [7, 16], it is assumed that the $A_{665}$ coefficient defines the content of compounds of high degree of humification. Higher values of that parameter were reported for the arable soils of the Chełmińskie Lakeland.

Indispensable information on the properties of humus substances is provided by the values of the absorbance ratios $A_{2/4}$, $A_{2/6}$, $A_{4/6}$ and the $\Delta \log K$ value [15, 16]. The value of the coefficient $A_{2/4}$ points to the presence of humus substance at its initial decomposition stage. In the arable-humus horizon of the Chełmińskie Lakeland soils there was found a slightly higher content of humus substance at the initial decomposition stage. The soil use method, both in the Chełmińskie Lakeland and the Krajeńskie Lakeland, did not show a considerable effect on the value of the $A_{2/4}$ coefficient. The $A_{2/6}$ coefficient points to the ratio of the content of compounds resistant to humification to strongly decomposed organic matter. It was noted that the soils of the Krajeńskie Lakeland under orchard-growing demonstrating acid reaction, contained more compounds resistant to humification. It was also found that arable soils of both mesoregions showed a higher content of compounds of a high degree of humification. The coefficient of $A_{4/6}$ is commonly applied to provide characteristics of humus compounds since with an increase in the molecular weight of humus compounds and polymerization of its aromatic nucleus the $A_{4/6}$ value decreases. For that reason the coefficient $A_{4/6}$ can serve as the indicator of the degree of humification. The humic acids isolated from arable soils of both the Krajeńskie Lakeland and Chełmińskie Lakeland demonstrated slightly lower values of that parameter, as compared with the HAs of soils in orchards. However, one cannot define them as humic acids of a greater condensation of aromatic rings in the molecules [9]. The advancement of the humification process Kumada [16] relates to the values of the $\Delta \log K$ coefficient. It was found that $\Delta \log K$ values were slightly higher for humic acids isolated from soils in orchards.

Susceptibility of humic acids to chemical oxidation

A relatively easy method of defining the susceptibility of HAs to oxidation is treating them with hydrogen peroxide (H$_2$O$_2$), which results in the destruction of the molecules of HAs, which leads to a decrease in the absorbance of the solutions analysed. Absorbance was measured at the wavelengths of 465 and 665 nm ($A_{U465}$, $A_{U665}$). The results were given as a percentage of the initial absorbance of the comparative solution ($\Delta A_{U465}$, $\Delta A_{U665}$). There was also calculated the value of the quotient $A_{U4/6}$. The results are presented in Table 4. A lower susceptibility to chemical oxidation was reported for the humic acids isolated from arable soils of both mesoregions. The changes in the value of absorbance of humic acids solutions after chemical oxidation are accompanied by changes in the value of the $A_{U4/6}$ coefficient. Gonet [4] showed that it is the aliphatic part, which is more susceptible
to chemical oxidation while it is the aromatic part, the molecules of HAs, which is
more resistant. The parameter has provided interesting information on the
structure of the humic acids analysed. There was reported a considerable decrease
in the value of that parameter after the chemical oxidation to humic acids of arable
soils of the Krajeñskie Lakeland, whereas the Che³miñskie Lakeland was
identified with the opposite trend. Higher differences in the value of \( \Delta_{U465/6} \)
parameter as a result of chemical oxidation point to a greater content of aliphatic
structures in the molecules of the HAs analysed. The present results suggest that
humic acids of arable soils of the Che³miñskie Lakeland showed a lower content of
aliphatic structures, while in the Krajeñskie Lakeland the HAs of arable soils
showed a greater content of aromatic structures, resistant to chemical oxidation. It
was observed that in the soils of slightly acid and acid reaction, the HAs showed a
greater resistance to chemical oxidation, which stands for an advantage of
aromatic structures in their molecules.

Soils in the Che³miñskie Lakeland orchards showed the highest humus
content, however, the HAs isolated from them did not show any essential
differences as compared with the HAs of the other samples. The analysed soils
were exposed to an intensive agricultural use. The acid reaction of soils in the
orchards of the Krajeñskie Lakeland and slightly acid reaction of arable soils of the
Che³miñskie Lakeland shows that throughout their long-term agricultural use no
liming was applied. The period of 30-year orchard cultivation and the application
of the herbicide in stripes, differentiated the properties of HAs inconsiderably.

Ward’s method applied in the cluster analysis was used to evaluate the distance
between the clusters. The cluster analysis of the results of the physicochemical
properties (Fig. 1) made it possible to separate two groups pointing to a slight

TABLE 4. SUSCEPTIBILITY ON CHEMICAL OXYGENATION HUMIC ACIDS

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \Delta_{U465} )</th>
<th>( \Delta_{U665} )</th>
<th>( \Delta_{U465} )</th>
<th>( \Delta_{U665} )</th>
<th>( \Delta_{U465/6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Che³miñskie Lake District</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1</td>
<td>0.20</td>
<td>0.04</td>
<td>64.10</td>
<td>55.55</td>
<td>5.00</td>
</tr>
<tr>
<td>K2</td>
<td>0.24</td>
<td>0.05</td>
<td>63.63</td>
<td>54.54</td>
<td>4.80</td>
</tr>
<tr>
<td>K3</td>
<td>0.34</td>
<td>0.09</td>
<td>60.00</td>
<td>50.00</td>
<td>3.77</td>
</tr>
<tr>
<td>K4</td>
<td>0.27</td>
<td>0.06</td>
<td>62.00</td>
<td>53.84</td>
<td>4.50</td>
</tr>
<tr>
<td>Krajeñskie Lake District</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tr</td>
<td>0.21</td>
<td>0.04</td>
<td>66.12</td>
<td>55.55</td>
<td>5.25</td>
</tr>
<tr>
<td>Wt</td>
<td>0.22</td>
<td>0.05</td>
<td>64.50</td>
<td>50.00</td>
<td>4.40</td>
</tr>
<tr>
<td>Ol</td>
<td>0.24</td>
<td>0.06</td>
<td>64.20</td>
<td>45.45</td>
<td>4.00</td>
</tr>
</tbody>
</table>
variation in the soil conditions in respective orchards and arable fields of the mesoregions. Based on the analysis of clusters of the results of the analyses of the properties of humic acids, there were also separated two groups (Figs 2, 3, 4). Small distances between groups point to a slight variation in the properties of humic acids. Slightly different were the properties of HAs of arable soils, as compared with the soils in orchards. The cluster analysis showed that despite varied physicochemical properties in the soil humus horizons in the orchards of both mesoregions, there were noted no considerable differences in the properties of HAs.
CONCLUSIONS

1. Humus substances of soils in the orchards showed a lower degree of condensation of aromatic rings in the molecules of humic acids, which points to a lower ‘chemical maturity’ of those compounds.

2. Similarly, soil management practices in the orchards decreased the resistance of humus substances to chemical oxidation. The humic acids isolated from those soils demonstrated a greater content of aliphatic structures.

3. Despite varied physicochemical properties in the soil humus horizons in the orchards of both mesoregions, the cluster analysis showed that, there were noted no considerable differences in the properties of humic acids.

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Fig. 3. The cluster analysis based on the absorbance coefficients of humic acids.

Fig. 4. The cluster analysis based on the susceptibility on chemical oxygenation of humic acids.
WYBRANE WŁAŚCIWOŚCI SUBSTANCJI HUMUSOWYCH W GLEBACH ORNYCH I UŻYTKOWANYCH SADOWNICZO


REFERENCES