Introduction

Research carried out during the past years on the effects of acidic precipitation has greatly increased our knowledge of the changes in the soil properties and our understanding of mechanisms of the soil degradation. The results obtained in studies on the interaction between organic matter and acidic solution in soils are often contradictory. Acid pollution of the environment is caused mainly by sulphur dioxide formed during the combustion of coal, peat and oil and evolves from sea water, volcano and at the decay of the organic matter. Sulphur oxides are carried into the air and with water form sulphuric acid. The resulting “acid rain” acidifies soil and watercourses. Many books and review articles have dealt with the different aspects of these problems [1−3, 5, 9, 12, 18, 24].

Humic acids (HAs) are the major extractable components of soil humic substances and are thought to be complex aromatic macromolecules with aminoacids, amino sugars, peptides, aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for humic acid contains free and bound phenol OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings [22]. HAs show polyfunctional and highly diverse structures, which enable these compounds to form ionic, hydrophobic and electron donor-acceptor interactions, respectively. Due to the presence of the various functional groups, they form strong complexes with heavy cations [28]. The order of bonding strength for a number of metal ions onto humic acids is Hg²⁺>Cu²⁺>Pb²⁺>Zn²⁺>Ni²⁺>Co³⁺ [10].

In the present complexation study, the zinc concentration was used as it occurred in the waste in the Central Sewage Work in Poznan. Zinc is a very good candidate for probing the different functional groups of HA that are likely to complex metals [8, 21, 27].
Simultaneously, major amounts of zinc in wastewater from mining and steel plants and from municipal wastewater are discharged to the water and streams that flow through the area. The zinc toxicity depends on the ionic form, pH of the environment and the salt where it is incorporated. Zinc sulphate is considerably more toxic than zinc chloride [6, 7, 13, 15, 17, 19, 20, 25, 27]. The acid deposition of soils changes the metal mobility and the ability of metal checking. The liberation of heavy cations into the environment causes the intoxication of roots, the decrease of the plant resistance to pests, diseases and the hazard of humane health [14, 16, 23].

The aim of this paper was to quantify the zinc release from its complexes with HA and migration within soil phases under the effect of acid rain on the basis of distribution of radioactive zinc concentration in particular soil phases before and after the simulated acid rain. We have used a simple model system consisting of Fluka HA, a sand layer and acid rain (diluted H₂SO₄) to simulate natural processes occurring in the soil layer.

**Methods**

**Materials and reagents**

- Fluka HA No 53680 series GA 11745 from Fluka Chemie AG, Swiss.
- Zinc oxide was activated in a nuclear reactor by neutrons and the final preparation contained ⁶⁵Zn with the specific activity of 1 MBq of zinc (radiochemical purity 99.9%). The activation was performed in the nuclear reactor at Świerk/Otwock using a neutron flux of \(1.2 \times 10^{13} \text{n/cm}^2\cdot\text{s}\) for 25 min. Two weeks after the activation, the irradiated zinc oxide contained for the most part only the ⁶⁵Zn nuclides (half-life period \(T_{1/2}=245\pm0.8\) days, emitting \(\gamma\) radiation of energy 1.118 MeV and \(\beta\) particles of energy 0.325 MeV).
- Sulphuric acid, pure for analysis from Polchem-Torun, Poland.
- Hydrochloric acid, pure for analysis from POCh-Lublin, Poland.
- Sulphuric acid, ¹³S radiolabelled, with a specific activity of 900 MBq and a half-life period \(T_{1/2}=87.9\) days, emitting \(\beta\) particles of energy 169.1 keV. The solution was prepared in Polatom, Świerk/Otwock, Poland.
- Buffers: pH=4.01±0.01, 7.00±0.01, 9.80±0.01 from Radiometer-Copenhagen.
- Quartz sand, 0.2 mm of particle-size distribution, hydrochloric acid or sulphuric acid conditioned.

**Apparatus**

**Radiometers**

Measurements of the \(\gamma\) radiation intensity of samples including the zinc radioisotope were carried out with a radiometer, type URS-3 (POLON-ALFA, Poland) with a scintillation detector NaI(Tl). Parameters: the working voltage 1020 V and 50 s time of the measurement.

The samples of ⁳⁵S were measured by a Geiger-Müller counter type BOH-45. Parameters: the working voltage 690 V and 100 s time of the measurement.

**Spectrophotometry**

The eluates of washed humic samples by H₂SO₄ were diluted 1:50 with redistilled water and the absorption spectrum in the ultra-violet region by a Jasco Corporation Spectrophotometer (Model V-550) was measured.

**IR spectroscopy**

IR measurements were carried out with a Bruker infrared-spectrometer (Model FT-IR). Spectra were recorded in the range 4000–400 cm⁻¹. Humic samples were measured as KBr pellets using 1.5 mg of HA and 200 mg of KBr.

**Elemental analysis**

The composition of humic samples was carried out with a Perkin-Elmer elemental analyser (Model CH 2400). Analysis of products was performed by gas chromatography.

**Radioisotope determination of zinc bonding in HA layer**

The zinc solution (0.2 g of ⁶⁵ZnO and 0.3 ml of concentrated HCl) was made up to 200 ml. The ⁶⁵ZnCl₂ solution (5 ml) of various pH was introduced into the column (Supelco, Inc. type 6-4752, Fig. 1) and stored for 48 and 72 h at 20°C (Fig. 2). The...
Model radioisotope experiments on the influence of acid rain on $^{65}$Zn binding with humic acid

Column packing contained 0.3 g of the quartz sand and 0.1 g of Fluka HA. The γ radiation of the solution was measured before and after the storage to calculate the zinc bonding. In experiments we used 5 ml of $^{65}$ZnCl$_2$ solution of pH 4.0 and 72 h of the complexation and the obtained results are presented in Fig. 2.

Determination of acid rain influence on $^{65}$Zn and HA layer

The zinc and HA layer was washed with a solution of H$_2$SO$_4$ of pH: 3.1, 4.2, 5.0 or 5.6. The elution was performed two times using 3 ml (the radiation minimum of the elution) of the acid solution each time. The volume stoppage of HCl and H$_2$SO$_4$ solutions on the sand at pH 4.2 and HA (wet or dry) were estimated to introduce a correction into the calculation. Hydrochloric acid was used to compare the influence of the inorganic acid with or without oxygen on humic acid, the complexation and the elution.

The samples for the determination of H$_2$SO$_4$ influence on Fluka HA were prepared after 72 h of the column storage. Humic acid (0.1 g) was introduced into the column with the quartz sand of 0.2 mm granules (0.3 g) and washed with 5 ml of H$_2$SO$_4$ at pH 3.0, 3.7, 4.2, 4.8 and 5.0. The UV spectra of eluates were measured by the spectrophotometer. The HA layers were analysed using IR spectroscopy and elemental analysis. The adsorption of sulphur and sulphur anion on HA and sand layer were tested by means of the $^{35}$S radionuclide and the Geiger-Müller radiometer.

Results and discussion

The acid rain influence on $^{65}$Zn and HA layer

On adding metal cations to the HA layer and the sand gave the stoppage degree of $^{65}$Zn on HA 52.5% and 10.3% on the sand. The IR spectra of HA and metal-loaded forms were measured with conventional techniques. The HA-Zn layer had the following absorption peaks: principal features 3300 cm$^{-1}$ (-OH asoc.), 1590 cm$^{-1}$ (COO- asym.), 1385 cm$^{-1}$ (COO-sym.) [4]. Peaks are characteristic for binding zinc-salicylic acid (or zinc-phthalic acid). These effects are consistent with metal binding by CO$_2$ functional groups, as concluded by others [11].

When the HA and zinc layer is washed with acid rain, any loosely bond metal is removed and only “tightly” bound metal remains. Adding these acid solutions at different pH to the solid HA and zinc layer inside the column with sand gave first (3 ml) the elution 1.87–4.86% of zinc (Table 1). The main elution of zinc was from the sand layer, the sponge.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$A_b$ (c/50 s)</th>
<th>$A_1$ (c/50 s)</th>
<th>$A_c$ (c/50 s)</th>
<th>$A_c$–$A_b$ (c/50 s)</th>
<th>Zinc binding (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand+HA+HCl addition of $^{65}$ZnCl$_2$</td>
<td>8043</td>
<td>3306</td>
<td>161</td>
<td>3145</td>
<td>60.90</td>
</tr>
<tr>
<td>Sand+HA+H$_2$SO$_4$ addition of $^{65}$ZnCl$_2$</td>
<td>7938</td>
<td>3967</td>
<td>100</td>
<td>3867</td>
<td>51.29</td>
</tr>
<tr>
<td>Sand+H$_2$SO$_4$ addition of $^{65}$ZnCl$_2$</td>
<td>8095</td>
<td>7582</td>
<td>143</td>
<td>7439</td>
<td>8.23</td>
</tr>
<tr>
<td>Sand+HCl addition of $^{65}$ZnCl$_2$</td>
<td>8118</td>
<td>7691</td>
<td>100</td>
<td>7591</td>
<td>6.49</td>
</tr>
</tbody>
</table>

Table 1. Results of zinc binding (a–c) and acid elution (d–h).

\[
\text{Elution}^* = \frac{e}{(a - b)} \times 100\%
\]

Table 2. Results of zinc binding after the acid degradation (pH 4.2) of HA layer.

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
\text{Samples} & A_b & A_1 & A_c & A_c - A_b & \text{Zinc binding} \\
\hline
\text{Sand+HA+HCl} & 8043 & 3306 & 161 & 3145 & 60.90 \\
\text{addition of }^{65}\text{ZnCl}_2 & & & & & \\
\text{addition of }^{65}\text{ZnCl}_2 & 7938 & 3967 & 100 & 3867 & 51.29 \\
\text{addition of }^{65}\text{ZnCl}_2 & 8095 & 7582 & 143 & 7439 & 8.23 \\
\text{addition of }^{65}\text{ZnCl}_2 & 8118 & 7691 & 100 & 7591 & 6.49 \\
\hline
\end{array}
\]

Fig. 3. The elution of $^{65}$Zn by H$_2$SO$_4$ with $^{65}$Zn+HA layer at different pH.

A$_b$ – radiation intensity of $^{65}$ZnCl$_2$ solution before the experiment, A$_1$ – radiation intensity of $^{65}$ZnCl$_2$ solution (eluate) after the experiment (72 h incubation), A$_c$ – volume stoppage of $^{65}$ZnCl$_2$ solution on analyzed layer, A$_c$–A$_b$ – radiation of $^{65}$Zn binding in HA layer, c/50 s – count per 50 s.
structure of HA and partly as a result of the zinc decomplexation. However, the layers were washed two times. The second portion of 3 ml, especially in the case of pH 3.1, caused a higher zinc elution than the first portion (2.46–9.58%). Figure 3 shows the elution of $^{65}$Zn by H$_2$SO$_4$ at different pH. An increase of acid rain amount and H$_2$SO$_4$ concentration inside of HA layers affects the degradation of HA, decomplexation of organic bonds between zinc and humic substances and the significant metal release.

Table 2 shows three sets of metal binding analytical data. The first is the maximum of zinc binding (60.9%) for Fluka HA washing with HCl at pH 4.2 and analysing the intensity of $\gamma$ radiation. The washing of HA with H$_2$SO$_4$ at pH 4.2 caused a lower the zinc binding than with HCl (51.29%). The results are shown in line 2 of Table 2. The sand binding of zinc was 6.49% after washing with HCl (line 3, Table 2) that is similar to the H$_2$SO$_4$ washing. Assuming that RCO$_2$H groups are the principal organic binding sites for Zn$^{2+}$ in the pH range 4.0–4.5 of our experiments, the data in Table 2 inform about the different influence of HCl and H$_2$SO$_4$ on Fluka HA and zinc binding with organic groups. The IR spectra of HA samples washed with H$_2$SO$_4$ included changes (a decrease in the absorbance) in the region: 3500–2750 cm$^{-1}$ (OH), 1500–1650 cm$^{-1}$ (C=O of carbonyl or COOH), 1385 and 1590 cm$^{-1}$ (COO asym. and COO- sym.), 1250 cm$^{-1}$ (C=S) and 400–500 cm$^{-1}$ (S-S) (Fig. 4). IR spectra of Fluka HA and HA washed with HCl are nearing. The UV absorbance of column eluates washed HA with H$_2$SO$_4$ and HCl (at pH 4.2) was properly 2:1 meaning that H$_2$SO$_4$ has a higher elution efficiency than HCl.

Figure 5 and Table 3 compare the UV absorbance of eluates from HA washed with H$_2$SO$_4$ of different concentrations. The solutions of H$_2$SO$_4$ were prepared in the pH range 3.1–5.5 at 20°C, typically for natural acid rain. The UV spectra of eluates indicate the different interaction of H$_2$SO$_4$ on Fluka HA. One can see that the maximum of the absorbance appears in the concentration range below 0.0001 mol/dm$^3$ of H$_2$SO$_4$ (an elution and soluble process of compounds of low molecular mass) and a uniform increase above 0.0001 mol/dm$^3$ (the degradation process of Fluka HA). The curves for 270, 400 and 550 nm run similarly. The data set in Table 4 there are respective element contents in HA washed with H$_2$SO$_4$ and

<table>
<thead>
<tr>
<th>pH</th>
<th>H$_2$SO$_4$ (mol/dm$^3$)</th>
<th>$\lambda$ (nm)</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>3.97-E04</td>
<td>270</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>0.005</td>
</tr>
<tr>
<td>3.6</td>
<td>1.25-E04</td>
<td>270</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>0</td>
</tr>
<tr>
<td>4.2</td>
<td>3.15-E05</td>
<td>270</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>0.004</td>
</tr>
<tr>
<td>4.8</td>
<td>7.92-E06</td>
<td>270</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>0.003</td>
</tr>
<tr>
<td>5.5</td>
<td>1.58-E06</td>
<td>270</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>0.007</td>
</tr>
</tbody>
</table>
HCl at pH 4.2. The amounts of C, H and N decrease about 40% after the action of H$_2$SO$_4$ while quite insignificantly after the HCl action. These effects testify to the large degradation of Fluka HA by H$_2$SO$_4$ (IR spectrum – Fig. 6).

In the radioisotope experiment using H$_2^{35}$SO$_4$ and the Geiger-Müller counter, it was proved that the HA stops 8% of sulphur only. This suggests that the SO$_4^{2-}$ anion possesses a high ability to decompose not only HA-Zn complexes, but also HA.

The product of H$_2$SO$_4$-HA+Zn complexes are water and acid soluble, as only 8% of the $^{35}$S residues is found in the HA-Zn-sand layer.

Conclusions

The experiments were performed in glass columns with the sand packing which can simulate natural conditions. The influence of acid rain on humic substances is drastic and washes zinc significantly. This degradation of humic layer may be probably explained by assuming the creation of hydrogen bonds by free electron pairs at oxygen atoms of the SO$_4^{2-}$ anion. Such an interaction has the low probability for HCl. Simultaneously, the weakening of these bonds in HA leads to its degradation. The increase of acid rain concentration affects the release and the zinc moves down the soil profile and can pollute surface or underground waters. An increase in the zinc mobility has important consequences of the soil acidification. According to our best knowledge, this is a significant report on the essential difference between HCl and H$_2$SO$_4$ interaction with HA. The decomplexation and the change of the humic solubility may enhance the biological availability and toxicity of Zn$^{2+}$ in soils. However, even more unexpected is a degradation power of H$_2$SO$_4$ towards HA and HA+Zn complexes.

It is well known that humic acids are insoluble in acidic solutions and this feature is used to separate humic substances into humic and fulvic acid fractions. This degradation by H$_2$SO$_4$ may also have the analytical consequence in the procedure of HA isolation when using HCl or H$_2$SO$_4$. The ecological consequences of acid rain rich in SO$_4^{2-}$ would be much more severe for humic substances than expected previously. It is important for humic acids of low molecular mass and the humification which often occur in the environment. Fluka humic acid has simulated this problem perfectly.

Acknowledgment

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References


Table 4. The elemental analysis of Fluka HA before and after the acid degradation (pH 4.2).

<table>
<thead>
<tr>
<th>Elemental samples</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluka I burning</td>
<td>45.33</td>
<td>4.04</td>
<td>0.72</td>
</tr>
<tr>
<td>II burning</td>
<td>45.25</td>
<td>3.96</td>
<td>0.71</td>
</tr>
<tr>
<td>Fluka – degradation I burning</td>
<td>32.22</td>
<td>2.70</td>
<td>0.48</td>
</tr>
<tr>
<td>II burning</td>
<td>27.81</td>
<td>2.70</td>
<td>0.44</td>
</tr>
<tr>
<td>H$_2$SO$_4$ III burning</td>
<td>27.10</td>
<td>2.20</td>
<td>0.36</td>
</tr>
<tr>
<td>Fluka – degradation I burning</td>
<td>45.65</td>
<td>4.23</td>
<td>0.71</td>
</tr>
<tr>
<td>II burning</td>
<td>44.66</td>
<td>4.07</td>
<td>0.69</td>
</tr>
<tr>
<td>HCl III burning</td>
<td>44.96</td>
<td>4.12</td>
<td>0.69</td>
</tr>
<tr>
<td>Fluka – degradation I burning</td>
<td>45.65</td>
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<td>0.71</td>
</tr>
<tr>
<td>II burning</td>
<td>44.66</td>
<td>4.07</td>
<td>0.69</td>
</tr>
</tbody>
</table>