

Model radioisotope experiments on the influence of acid rain on ^{65}Zn binding with humic acid

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Abstract Acid rain formed first of all from sulphur oxide emitted by natural and anthropogenic sources, may change the biological equilibrium and the metal stoppage in the soil. The model experiments were performed to determine the influence of acid rain on zinc bond with humic acid (HA). The samples were prepared in glass columns with quartz sand and overlaid HA or HA+ ^{65}Zn radioisotope that simulates natural conditions. Then, solutions of H_2SO_4 were introduced into the sand – HA layer. Zinc was washed with diluted (10^{-4} – 10^{-3} M) sulphuric acid as the simulation of acid rain. The recovery of injected radiotracer ions in eluates was found to depend on pH of simulated acid rain. The results help to evaluate the migration behaviour of zinc in the presence of HA and H_2SO_4 . The model studies illustrate the considerable influence of sulphuric acid on chemical degradation of HA.

Key words acid rain • complexation • humic acid • sulphuric acid • zinc

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 $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$ [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].

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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 considerable 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 H_2SO_4) 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 ^{65}Zn 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 1.2×10^{13} n/cm²·s for 25 min. Two weeks after the activation, the irradiated zinc oxide contained for the most part only the ^{65}Zn nuclides (half-life period $T_{1/2} = 245 \pm 0.8$ days, emitting γ radiation of energy 1.118 MeV and β particles of energy 0.325 MeV).
- Sulphuric acid, pure for analysis from Polchem-Toruń, Poland.
- Hydrochloric acid, pure for analysis from POCh-Lublin, Poland.
- Sulphuric acid, ^{35}S radiolabelled, with a specific activity of 900 MBq and a half-life period $T_{1/2} = 87.9$ days, emitting β 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 γ 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 ^{35}S were measured by a Geiger-Müller counter type BOH-45. Parameters: the working voltage 690 V and 100 s time of the measurement.

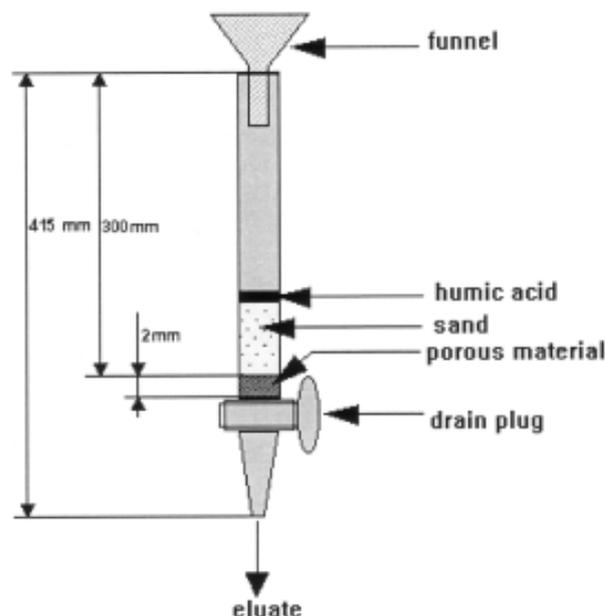


Fig. 1. The separation column of $\varnothing=13$ mm.

Spectrophotometry

The eluates of washed humic samples by H_2SO_4 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 ^{65}ZnO and 0.3 ml of concentrated HCl) was made up to 200 ml. The $^{65}ZnCl_2$ 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

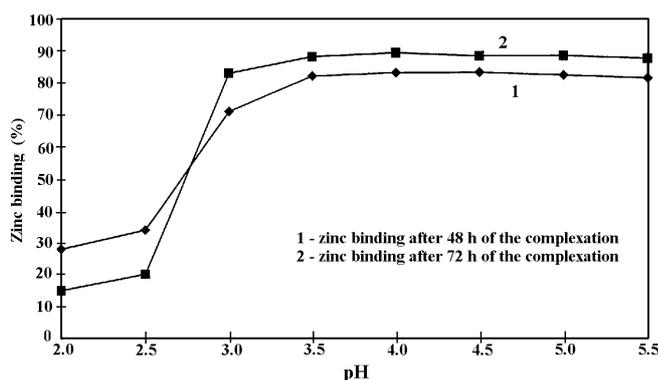


Fig. 2. The curves of the complexation for zinc and HA.

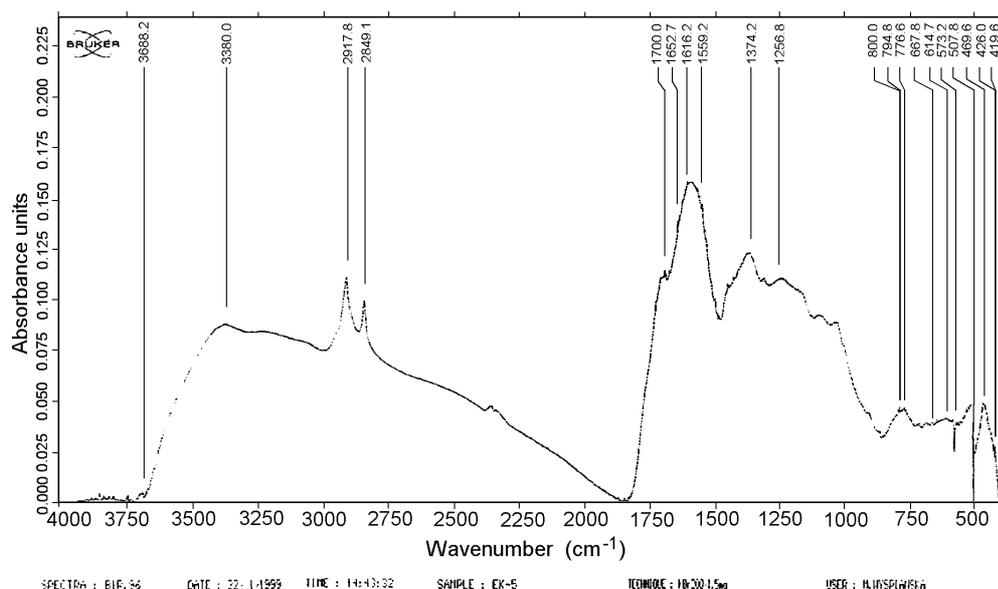


Fig. 4. IR spectrum of Fluka HA.

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 $^{65}\text{Zn}^{\text{II}}$ by H_2SO_4 at different pH. An increase of acid rain amount and H_2SO_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 γ radiation. The washing of HA with H_2SO_4 at pH 4.2 caused a lower 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_2SO_4 washing. Assuming that RCO_2^- groups are the principal organic binding sites for Zn^{II} 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_2SO_4 on Fluka HA and zinc

binding with organic groups. The IR spectra of HA samples washed with H_2SO_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_2SO_4 and HCl (at pH 4.2) was properly 2:1 meaning that H_2SO_4 has a higher elution efficiency than HCl.

Figure 5 and Table 3 compare the UV absorbance of eluates from HA washed with H_2SO_4 of different concentrations. The solutions of H_2SO_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_2SO_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_2SO_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_2SO_4 and

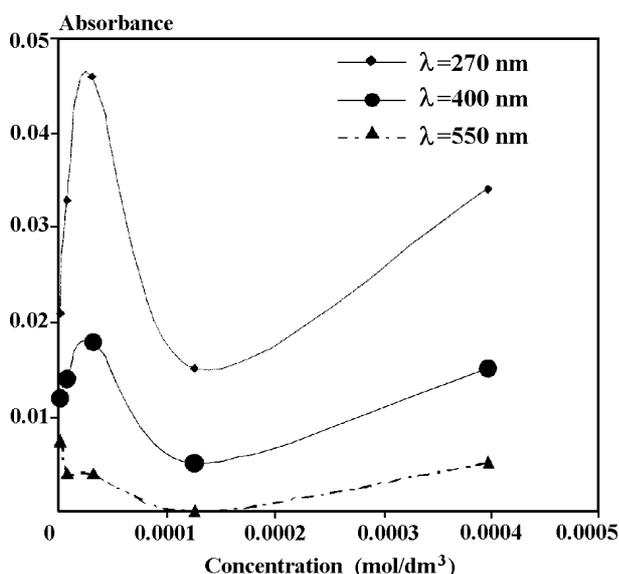
Fig. 5. UV absorbance of eluates (diluted 1:50) after HA washing with H_2SO_4 of different concentrations.

Table 3. The absorbance of eluates after the acid degradation of HA.

pH	H_2SO_4 (mol/dm^3)	λ (nm)	A
3.1	3.97-E04	270	0.034
		400	0.017
		550	0.005
3.6	1.25-E04	270	0.012
		400	0.005
		550	0
4.2	3.15-E05	270	0.046
		400	0.017
		550	0.004
4.8	7.92-E06	270	0.033
		400	0.014
		550	0.003
5.5	1.58-E06	270	0.021
		400	0.017
		550	0.007

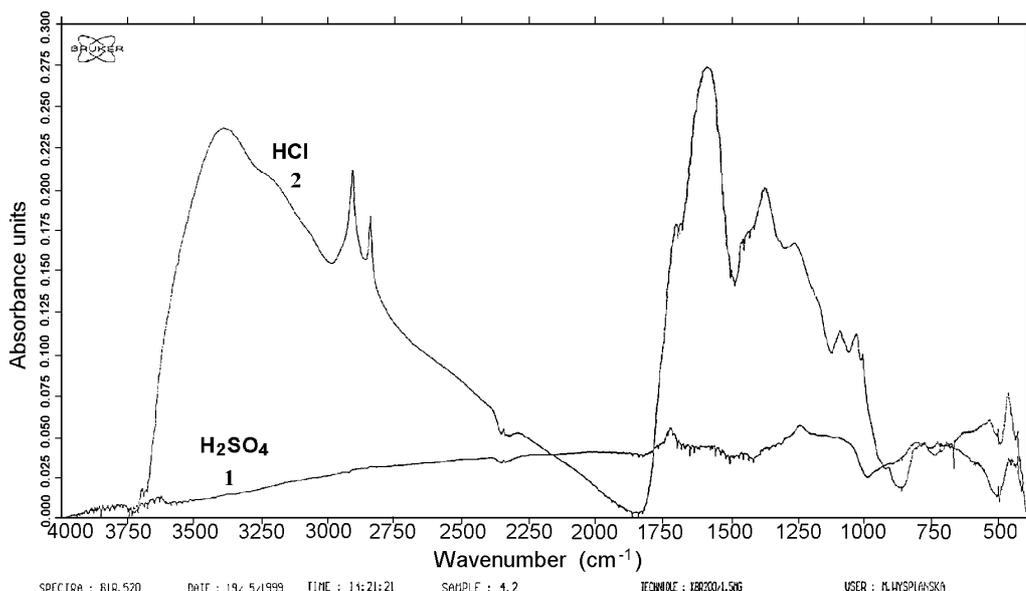


Fig. 6. IR spectrum of Fluka HA eluted with H₂SO₄ (1) or HCl (2).

HCl at pH 4.2. The amounts of C, H and N decrease about 40% after the action of H₂SO₄, while quite insignificantly after the HCl action. These effects testify to the large degradation of Fluka HA by H₂SO₄ (IR spectrum – Fig. 6).

In the radioisotope experiment using H₂³⁵SO₄ and the Geiger-Müller counter, it was proved that the HA stops 8% of sulphur only. This suggests that the SO₄²⁻ anion possesses a high ability to decompose not only HA-Zn complexes, but also HA.

The product of H₂SO₄-HA+Zn complexes are water and acid soluble, as only 8% of the ³⁵S 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 SO₄²⁻ 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 H₂SO₄ interaction with HA. The decomplexation and the change of the humic solubility may enhance the biological availability and toxicity of Zn²⁺ in soils. However, even more unexpected is a degradation power of H₂SO₄ 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 H₂SO₄ may also have the analytical consequence in the procedure of HA isolation when using HCl or H₂SO₄. The ecological consequences of acid rain rich in SO₄²⁻ 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.

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

Elemental samples		C (%)	H (%)	N (%)
Fluka	I burning	45.33	4.04	0.72
	II burning	45.25	3.96	0.71
Fluka – degradation	I burning	32.22	2.70	0.48
	II burning	27.81	2.70	0.44
H ₂ SO ₄	III burning	27.10	2.20	0.36
Fluka – degradation	I burning	45.65	4.23	0.71
	II burning	44.66	4.07	0.69
HCl	III burning	44.96	4.12	0.69

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