

## Investigation of iron status in Terric Histosols

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*Received February 12, 2002; accepted March 25, 2002*

**A b s t r a c t.** The iron status in 14 differently transformed muck formations (Terric Histosols) was studied. The Moessbauer spectra showed that most of the iron in all the samples was trivalent. An attempt to find the relationship between the iron content and the state of the soil transformation was performed. The w/w percentage of the total iron as well as the (alkaline extractable) organic iron increased with the increase of the ratio of humic to fulvic acids.

**K e y w o r d s:** iron, mucks, humic and fulvic acids ratio

### INTRODUCTION

Poland has about  $2 \cdot 10^6$  ha of organic soils mostly developed from peat. After drainage, the peat undergoes transformation under aerobic conditions which leads to the formation of muck. This transformation is a set of simultaneous complex processes among which mineralization and secondary humification are of the greatest importance. During transformation, changes in chemical and physical soil properties occur. Taking into account the degree of the peat transformation, the muck mass can be divided into three categories:  $Z_1$  - peaty muck,  $Z_2$  - humic muck and  $Z_3$  - proper muck (Okruszko, 1976). In the peat-muck soil, the muck constitutes the upper part and primary peat the lower part of the profile. The thickness of the muck layer depends on the intensity of drainage. Based on the thickness of this layer, peat-muck soils are next divided into three groups, weakly transformed (MtI), medium transformed (MtII) and strongly transformed (MtIII) (Okruszko, 1976).

Iron plays a vital role in soil formation and in the dynamics and fate of nutrients and pollutants in the environment. The accumulation of iron in mucks is mainly the effect of the mineralization of organic matter and depends on the overall bioecological conditions of the soil including precipitation of  $Fe^{+3}$  from surface and groundwater (Piaścik, 1996). The effect of pedogenetic environments on the nature

of iron oxide formed in mineral soils has been the subject of many studies (Schwertmann, 1985; Singer and Fine, 1989). Soil environmental factors, which influence the modes of formation of Fe oxides, include the initial valence of the iron source, its concentration in soil solution, the rate of oxidation of Fe (II), and parameters such as pH, Eh, temperature, soil moisture, soil organic matter, activity of Al and other ionic factors, e.g., inorganic cations and anions, and organic ligands. The role of organics in iron oxide transformation is very important (Huang and Wang, 1997). In soil environment where the amount of organic matter is low (for example in subsoils), the Fe supplied will form goethite and hematite depending on the environmental factors. As the organic matter content increases, more of the Fe will be completed with organics leading to decreases of Fe activity. This would not allow the formation of hematite but only of goethite. With a higher content of organic matter, the rate of Fe supply is high, ferrihydrite will form and survive even for pedogenic times (Singer and Fine, 1989). If the content of organic matter is even higher, such as in O horizons or in peaty environments, all of the Fe may be in the form of Fe-organic complexes. However, there is still a lack of studies on the distribution of iron in organic soils (Norrstrom, 1995).

The hypothesis of our work was that the iron content, and the distribution of its forms, reflect the intensity of the mucking processes. Selected chemical and physical analyses of fourteen samples have been carried out to study the iron status in mucks.

### MATERIALS AND METHODS

The study was conducted on muck samples taken from the upper layers of 14 differently transformed peat-muck

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profiles located on grasslands in the Polesie Lubelskie region and Biebrza river valley. The studied samples were taken from depths of 5-10, 5-15 and 5-25 cm, depending on the mucking stage. All the samples originated from soils utilised for grassland. The samples were classified as peaty-mucks -  $Z_1$  and proper (granulated) mucks -  $Z_3$ . Table 1 shows selected physical properties of the investigated soils together with the composition of humic substances (Bambalov *et al.*, 1998; Lishtvan *et al.*, 2000).

The total content of iron in the investigated mucks was determined using the AAS method. The results were expressed as the percentage of  $Fe_2O_3$  in 105°C dry soil.

The mineral forms of iron were studied by  $^{57}Fe$ -Moessbauer spectroscopy based on the effect of the recoilless emission and absorption of  $\gamma$  radiation by nuclei in solids (Wertheim, 1964; Verret, 1980). The Moessbauer spectroscopy is specific for iron, so iron bearing compounds of low concentrations may be analysed without the spectral interference of other minerals. This method can be used to study finely dispersed and/or poorly crystalline materials (Babanin, 1973). The Moessbauer spectrum of an iron mineral is its characteristic feature and, with proper interpretation and under suitable conditions, this can be used as a mineral 'fingerprint' (Murad, 1988). Room temperature Moessbauer spectra were obtained using an MS1101E spectrometer with a constantly accelerating drive system ( $^{57}Co/Cr$  source with an activity of about 32 mCi). The velocity scale was calibrated using iron and sodium nitroprusside. From the Moessbauer spectra relative amounts of total and divalent iron were estimated numerically using the UNIV (Dubowcew *et al.*, 1990) program.

The determination of iron connected with organic matter,  $Fe_{org}$ , was carried out in alkaline extracts using the

AAS method. The results were expressed as w/w percentage of  $Fe_2O_3$  in 105°C dried soil. The alkaline extracts of organic matter were obtained by 0.45  $\mu m$  filtering of the supernatants from suspensions of homoionic hydrogen forms of fresh muck materials (containing exactly 0.4 g of dry organic matter) treated by NaOH solutions at pH = 10 at 1:100 w/w solid to liquid ratio.

## RESULTS AND DISCUSSION

The data related to the iron status in the investigated peat-muck soils is summarized in Table 2.

The studied soils contain from 0.24% (sample No. 13) to 2.82% (sample No. 5) of  $Fe_2O_3$ . The obtained values of %  $Fe_{org}$  ranged between <0.01 and 0.14. The relative content of  $Fe^{+2}$  in the total iron is rather low (less than 2.7%).

The shape of the Moessbauer spectra is similar for all studied mucks. In all cases the kind of obtained spectra was similar. Figure 1 shows the example of Moessbauer spectra for samples Nos 12 and 9. An area under the peaks reflects the bulk content of Fe (in relative units). The divalent iron (if present) forms a peak around 1.2 -1.5  $mm s^{-1}$ . The latter peak is nearly absent in all studied mucks which reflects that most of the iron in all the samples is trivalent. This indicates that in the studied peat-muck soils the amorphous oxides of trivalent iron dominate.

An attempt to find the relationship between the iron content and the state of the soil transformation was undertaken. As the advancing process of secondary humification in the upper 0-30 cm layer of muck soils was clearly illustrated by the ratio of humic to fulvic acids, we should use such iron characteristics which are in correlation with the humic and fulvic acids ratio (HA/HF). It is widely accepted that the

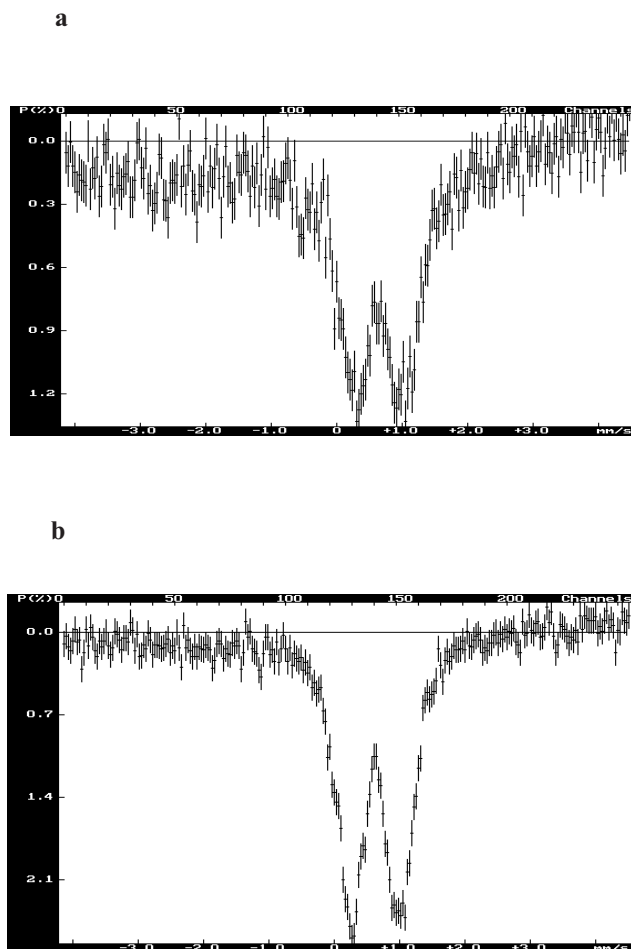
**Table 1.** Physical properties of the investigated soil samples together with the contents of fulvic acids and humic acids

No.	Kind of moorsh	HF (%)	HA (%)	Ash content (% d.m)	Bulk density ( $g cm^{-3}$ )	Total porosity (vol. %)	pH	
							H <sub>2</sub> O	1N KCl
1	$Z_1$	8.09	15.62	17.56	0.25	84.6	5.48	5.18
2	$Z_3$	6.66	33.63	18.03	0.36	77.8	4.95	4.49
3	$Z_3$	7.09	30.94	37.81	0.46	74.9	5.17	4.64
4	$Z_3$	12.75	29.31	15.80	0.31	80.9	5.70	5.32
5	$Z_3$	7.93	29.94	22.27	0.39	78.7	5.54	5.00
6	$Z_3$	8.06	27.16	20.52	0.32	82.5	5.38	4.93
7	$Z_3$	9.38	32.75	16.26	0.28	82.7	4.75	4.23
8	$Z_3$	11.67	24.55	22.77	0.30	83.6	6.15	5.75
9	$Z_3$	9.60	26.84	18.94	0.31	80.9	5.45	4.97
10	$Z_3$	10.18	31.98	21.24	0.34	81.4	5.44	4.97
11	$Z_1$	8.71	31.12	20.54	0.28	84.7	4.72	4.23
12	$Z_1$	8.84	29.82	22.69	0.21	88.5	5.13	4.54
13	$Z_1$	11.49	14.40	15.14	0.24	85.2	5.84	5.33
14	$Z_3$	12.33	21.95	21.47	0.29	84.1	5.78	5.33

HF - fulvic acids, HA - humic acids,  $Z_1$  - peaty muck,  $Z_3$  - proper muck.

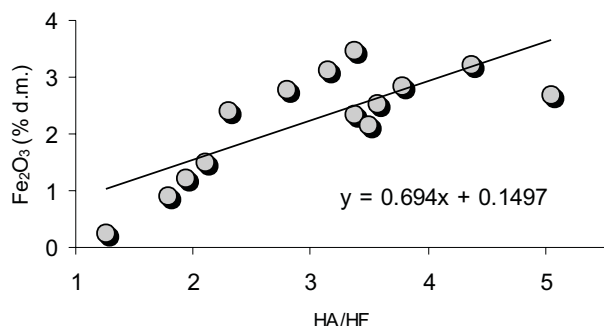
**Table 2.** Iron characteristics of the investigated peat-muck soils

No.	Type of muck	Fe <sub>2</sub> O <sub>3</sub> (% d.m.)	Iron content (relative unit)	Fe <sub>org</sub> (% d.m.)
1	Z <sub>1</sub>	1.22	0.8	0.01
2	Z <sub>3</sub>	2.68	1.4	0.14
3	Z <sub>3</sub>	3.23	1.3	0.11
4	Z <sub>3</sub>	2.42	1.0	0.05
5	Z <sub>3</sub>	2.83	1.8	0.08
6	Z <sub>3</sub>	2.78	2.6	0.03
7	Z <sub>3</sub>	2.17	1.4	0.11
8	Z <sub>3</sub>	1.50	1.2	0.04
9	Z <sub>3</sub>	3.47	2.2	0.14
10	Z <sub>3</sub>	3.13	1.8	0.10
11	Z <sub>1</sub>	2.53	1.4	0.13
12	Z <sub>1</sub>	2.34	1.3	0.06
13	Z <sub>1</sub>	0.24	<0.2	0.01
14	Z <sub>3</sub>	0.91	0.2-0.3	0.00

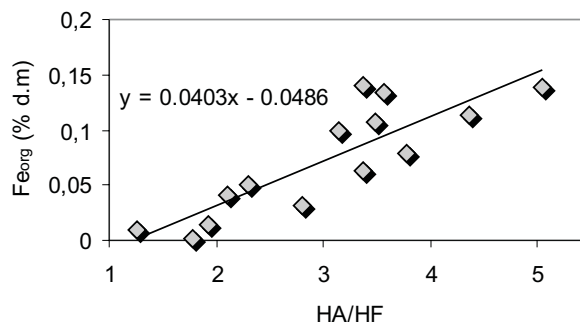
**Fig. 1.** The Moessbauer spectra for samples Nos 12 (a) and 9 (b).

forming of humic acids is the next step after the formation of fulvic acids and the higher the HA/HF ratio the more advancing the process of secondary humification. As a result of secondary humification, both the participation of fulvic acids and the fraction of low molecular weight components in humic and fulvic acids decreases. An increase in the amount of the total iron (%Fe<sub>2</sub>O<sub>3</sub>) with the increase of the ratio of humic to fulvic acids (HA/HF) was observed (Fig. 2).

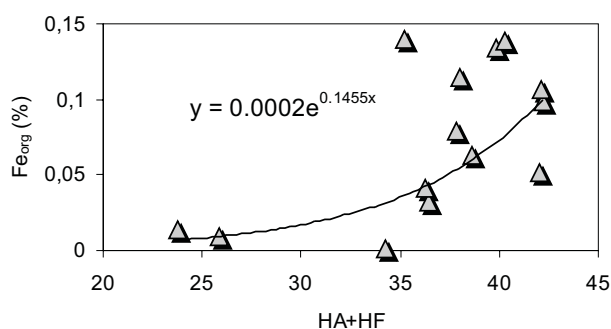
The process of secondary humification is accompanied by mineralization of organic matter. As the mucking process progresses under aerobic conditions, the amount of organic compounds with a high molecular weight (such as humic acids) increases, because these are less oxidizable. The resulting enrichment of the soil with humic acids, which are able to form stable Fe-organic matter complexes, means that the higher degree of humification is reflected in the increase of total iron content. Therefore the increase in the iron content reflects the progress of transformation of the studied soils. To verify that observation, it has been suggested that the organic iron (Fe<sub>org</sub>) is controlled by complexation with organic matter (OM). This is in agreement with other studies (Nissenbaum and Swaine, 1976) which have shown that Fe (along with Cu, Ni, Co, Zn) are associated with DOC in the pore waters of Saanich Inlet sediments. Alkaline organic matter extracts were used in this study to indicate that a significant fraction of iron is organically bound. There does not appear to be a simple relationship between Fe<sub>org</sub> and the total content of humic matter (HA+HF) (Fig. 3). The large increase of measurable - Fe<sub>org</sub> versus HA+HF suggests that the total content of humic matter is not a good measure of the concentration of chelate-organic complexes with iron. There was also no observed correlation (Krom and Sholkovitz,



**Fig. 2.** The content of total iron ( $\text{Fe}_2\text{O}_3$  (% d.m.)) versus humic to fulvic acids ratio (HA/HF).



**Fig. 4.** The content of organic iron ( $\text{Fe}_{\text{org}}$  (% d.m.)) versus humic to fulvic acids ratio (HA/HF).



**Fig. 3.** The content of organic iron ( $\text{Fe}_{\text{org}}$  (% d.m.)) versus the total content of humic matter (HA+HF).

1976) between the total dissolved Fe and DOC. For example, in their study it had been noted that that 15-40% of dissolved iron was bound to acid precipitated humic acid which constitutes less than 1% of the total DOC.

Regarding the amount of iron present in the organic matter extracts,  $\text{Fe}_{\text{org}}$  exhibits a positive correlation with the ratio of humic to fulvic acids as well, which is shown in Fig. 4. The presence of iron in alkaline extracts indicates that iron forms stable compounds with the organic matter of the studied mucks. The electrostatic attraction of positively charged surfaces of finely dispersed iron (III) oxides and negatively charged surfaces of humic acids may be one of the important mechanisms of the above phenomenon. The presence of iron in alkaline extracts indicates that the iron in mucks forms stable complexes with organic matter (Sapek and Sapek, 1987). It is well known that iron can form stable complexes with a range of organic ligands, including such functional groups that are widely present in humic and fulvic acids. Both the above binding mechanisms means that much of iron in the studied muck soils may occur as organic matter (especially humic acids) associates.

The importance of soil organic matter as the major factor in controlling the physical and chemical properties of soils has been recognized and the ability of soil organic matter to form complexes with metal cations has been well established (Sposito, 1989; Theng, 1974). A humus metal-binding ability seems to play an essential role in iron retention in the investigated peat-muck soils. Our studies indicate that iron is mainly associated with humic acids of peat-muck soils.

## CONCLUSIONS

1. The Moessbauer spectroscopy can be used to establish the iron characteristic of peat-muck soils.
2. The trivalent iron dominates in peat-muck soils.
3. The iron compounds in peat-muck soils form stable associates with humic acids.
4. The amount of total iron and organic iron increase with an advance of the process of mucking expressed by the increase of the ratio of humic to fulvic acids.

## ACKNOWLEDGMENTS

Authors would like to thank Dr. Andrey Alekseev and Dr. Tanya Alekseeva from the Institute of Physico-Chemical and Biological Problems in Soil Science, Russian Academy of Sciences, Pushchino, Moscow Region for investigating the studied soils by Moessbauer effect spectroscopy method.

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