Acta Agrophysica, 2001, 51, 215-220

EFFECT OF VARIOUS ORGANIC FERTILISERS ON THE HEAVY METAL FRACTIONS IN THE SOIL
Part 3. ZINC, MANGANESE AND IRON

B. Filipek-Mazur, K. Gondek

Department of Agricultural Chemistry, Agricultural University of Cracow
Mickiewicza 21, 31-120 Krakow, Poland

A b s t r a c t. The paper presents distribution of zinc, manganese and iron in fractions of soil treated with tannery sludge and compost of tannery sludge and peat, and, for the sake of comparison, the soil from a plot treated with farmyard manure (FYM), and mineral fertilisers.

Total soil contents of zinc ranged from 38.0 to 47.3 mg kg^{-1} of soil. The share of mobile zinc forms ranged between 6.05-7.93%. Percentage of the exchangeable form was between 5.8-7.5% of the total Zn contents, while the share of forms bound with organic matter ranged between 10.7 and 12.7%. A considerable part of zinc was bound with manganese and iron oxides. Between 30.14-43.72% of Zn were found in the residual form.

Organic and mineral treatment influenced the share of easily soluble manganese compounds. It ranged between 15.6-19.7%. The least of manganese (1.0-2.0%) occurred in the compounds with crystalline iron oxides. The exchangeable form constituted between 3.4-4.2%, organic fraction accumulated slightly more. Manganese oxides retained the most of the element.

Trace amounts of iron were revealed in the first three fractions. The biggest part of this metal was found in sparingly soluble compounds, mainly oxides (over 40%) and on residual fraction (over 30%).

K e y w o r d s: soil, organic material, chemical extraction, zinc, manganese, iron.

INTRODUCTION

Organic fertilisation is one of the ways to supplement nutrients in soil. A decreasing population of farm animals caused by the recession in agriculture considerably affects production of basic organic fertiliser, i.e. farmyard manure. Thus it becomes necessary to use higher amounts of other fertilisers containing big amounts of organic matter and nutrients indispensable for plants [1,2,6,13]. Organic industrial and communal wastes are the source that has not been exploited sufficiently so far. However, the use of those materials as fertilisers is limited by the contents of elements or substances harmful for the soil environment. Beside chemical substances, wastes may provide a sanitary hazard, i.e. contain considerable amounts of parasites and disease microorganisms, such as *Salmonella*, *Clostridium perfringenes* or *Ascaris* eggs [15]. We may limit the numbers of disease microorganisms through pasteurisation, fermentation, liming or composting, but limiting the heavy metal contents is a far more complicated procedure [5,7,17]. Sanitary requirements for sewage sludge concerning their heavy metal contents may be fulfilled when these materials have been properly processed. One of such processes is composting applied to sludge from a tannery sludge treatment plant. Apart from chromium, they do not threaten with contamination by other metals. Application of materials which originate from industry, including composts of tannery sludge, make monitoring of changes occurring in the soil after their application necessary. It is mainly due to the total contents of heavy metals and their distribution in individual compound fractions.

The aim of the present investigations was to determine changes in the contents and distribution of zinc, manganese and iron.

MATERIALS AND METHODS

Description of methods and properties of materials used for the experiment, as well as a detailed characteristics of the soil were presented in part I of this paper.

After fous years of the experiment, forms of Zn, Mn and Fe compounds were assayed in the average soil samples from individual experimental plots (Table 1) using the Zeien and Brummer's sequential chemical extraction method [18]. The following fractions were considered: F_1 - mobile, F_2 - exchangeable, F_3 - attached to manganese oxides, F_4 - attached to organic matter, F_5 - attached to poorly crystallised iron oxides, F_6 - attached to fully crystallised iron oxides, F_7 - residual (for the description of extraction see part I).

RESULTS AND DISCUSION

Total soil zinc contents decreased in relation to the control soil on the untreated plot after organic treatment (Table 1). The highest content of this metal, similar to that in the control samples, was detected in the soil treated with NPK mineral fertilisers (double dose - 47.3 mg kg^{-1}). Zinc belongs to more dynamic elements in the soil environment because of a relatively big share of the mobile exchangeable form. It is linked with manganese oxides and organic matter. Application

Table 1. Percentage distribution of zinc fractions in total Zn content in air-dry soil

Fertilizer object	Total concentration (mg kg^{-1})**	Contribution of particular fractions (%)						
		F_1	F_2	F_3	F_4	F_5	F_6	F_7
No fertilization	47.0	6.0	4.7	7.4	10.7	14.9	12.6	43.7
FYM I*	44.4	6.8	4.4	7.5	10.7	16.3	14.7	39.6
FYM II*	40.0	6.0	7.4	8.6	11.7	17.2	14.8	33.3
Peat compost I*	38.9	6.3	7.0	8.4	11.4	17.0	12.8	37.4
Peat compost II*	39.4	6.8	7.5	9.0	12.2	16.5	13.4	35.1
Sludge I*	40.7	7.9	6.2	8.3	11.9	17.2	13.6	36.0
Sludge II*	40.3	6.2	5.8	8.8	11.8	17.0	12.2	36.5
Mineral fertilization I*	39.8	7.2	5.2	8.0	12.8	17.9	14.2	35.8
Mineral fertilization II*	47.3	7.2	6.3	7.7	10.8	13.7	24.1	30.1

* I - single dose, II - double dose; ** sum of fraction F_1 - F_7.

of peat compost and raw sludge caused a slight increase in the percentage of mobile zinc forms (in relation to the control soil). The values ranged between 6.2 and 7.9% of the total contents. The proportion of the exchangeable form was similar (5.8-7.5% of total Zn contents). Kabata-Pendias [10] stated an increase in the zinc mobile forms share after introduction of municipal wastes.

The share of forms attached to organic matter (10.7-12.7%) in the soils of all the treatments remained on the level close to the value determined in the control soil (10.7%). A considerable portion of zinc was linked with manganese and iron oxides, which was mentioned also by other authors [4,8]. Mineral and organic fertilisation caused a decrease in permanent forms of zinc.

The applied organic and mineral treatment increased the share of easily water soluble manganese combinations in the soil, i.e. the mobile fraction (Table 2) but did not change proportions of other fractions in total contents of this element much. Mercik *et al.* [14] stated similar dependencies in their investigations on the effect of long-term mineral and organic fertilisation on the microelement contents in the soil. The share of mobile manganese was between 15.6% in the soil treated with peat compost (single dose) and 19.7% of total contents in the soil fertilised with mineral fertilisers. The lowest amount of manganese (total 1.0-2.0%) occurred in the combinations with crystalline iron oxides, which proved that this metal has high mobility which was also confirmed by other studies [12]. The exchangeable form constituted between 3.4-4.2% of the total Mn, organic fractions accumulated slightly more (5.4-6.5%) of it. Manganese oxides (F_3) retained the highest amounts of this element, and there Mn share ranged between 48.5-54.7%

Table 2. Percentage distribution of manganese fractions in total Mn content in air-dry soil

Fertilizer object	Total concentration (mg kg^{-1})**	Contribution of particular fractions (%)						
		F_1	F_2	F_3	F_4	F_5	F_6	F_7
No fertilization	758.6	15.0	3.6	52.4	6.2	17.8	1.8	3.3
FYM I*	705.5	18.5	3.8	49.0	5.6	17.6	2.0	3.4
FYM II*	756.0	16.4	4.2	49.5	5.6	15.7	1.8	2.7
Peat compost I*	806.2	15.6	3.5	54.0	6.3	15.7	1.3	2.8
Peat compost II*	819.6	17.8	3.5	54.7	6.2	15.6	1.7	2.7
Sludge I*	763.5	18.4	3.4	49.9	6.5	17.6	1.7	3.1
Sludge II*	713.2	17.5	3.5	52.2	5.4	15.3	1.7	3.4
Mineral fertilization I*	707.1	19.7	3.9	50.1	6.0	17.7	1.7	3.1
Mineral fertilization II*	639.1	19.7	3.5	48.5	6.2	17.2	1.0	3.9

* I - single dose, II - double dose; ** sum of fraction F_1 - F_7.

of total contents. The above data show that manganese and iron oxides played the greatest role in the manganese retention, as confirmed by Karczewska [11]. Irrespective of the applied treatment, the total amount of this metal changed slightly in comparison to the untreated control soil.

The studied soil, like the most soils in Poland, contained considerable amounts of iron [10]. Total content of this metal was lower in the soils after treatment than in the control soil (Table 3). The contents ranged between 1.2-1.5% Fe. There were trace amounts of this metal in the mobile and exchangeable fractions, while iron linked with manganese oxides constituted on average 0.4% of total Fe. The basic amount of the element falls to sparingly soluble combinations mainly attached to iron oxides and on the residual fraction. Over 60% was in the fraction linked with iron oxides, while the residual fraction accumulated up till 36.45% of the total iron. The obtained results are characteristic of this metal and were confirmed in other works [9,11].

CONCLUSIONS

1. Fertilisation with raw tannery sludge and compost based on it, did not cause any excessive accumulation of Zn, Mn and Fe in soil, or any major changes in their fractional distribution.

2. Zinc occurred in the residual fraction, while manganese in the fraction attached to manganese oxides.

3. Iron was characterised by a very low share in the easily soluble fractions, it concentrated in the combinations with iron oxides and in the residual fraction.

Table 3. Percentage distribution of iron fractions in total Fe content in air-dry soil

Fertilizer object	Total concentration (mg kg^{-1})**	Contribution of particular fractions (%)						
		F_1	F_2	F_3	F_4	F_5	F_6	F_7
No fertilization	15915	0.03	0.01	0.41	5.93	48.79	14.01	30.82
FYM I*	14837	0.04	0.02	0.46	5.66	45.73	17.73	30.36
FYM II*	14208	0.03	0.02	0.50	6.13	47.65	18.51	27.17
Peat compost I*	13828	0.02	0.04	0.41	6.49	45.31	16.96	30.77
Peat compost II*	15176	0.03	0.03	0.40	5.95	47.80	17.76	28.04
Sludge I*	15856	0.02	0.02	0.36	5.68	52.22	13.15	28.54
Sludge II*	13424	0.03	0.05	0.43	5.68	44.40	17.06	32.37
Mineral fertilization I*	12842	0.04	0.04	0.44	6.83	43.61	18.14	30.91
Mineral fertilization II*	12044	0.04	0.04	0.54	6.64	44.71	11.58	36.45

* I - single dose, II - double dose; ** sum of fraction F_1 - F_7.

REFERENCES

1. **Baran S., Bielińska J., Wiśniewski J.:** Wpływ stosowania niekonwencjinalnych nawozów wieloskładnikowych na wybrane właściwości gleby lekkiej. Zesz. Nauk. AR Szczecin, 72, 11-20, 1998.
2. **Baran S., Flis-Bujak M., Turski R., Żukowska G.:** Zmiany właściwości fizykochemicznych gleby użyźnionej osadem ściekowym. Roczn. Glebozn., 47, 3-4, 123-130, 1996.
3. **Baran S., Turski R.:** Degradacja, ochrona i rekultywacja gleb. Wyd. AR Lublin, 1996.
4. **Chłopecka A.:** Wpływ różnych związków kadmu, miedzi, ołowiu i cynku na formy tych metali w glebie oraz na ich zawartość w roślinach. Wyd. IUNG, Puławy, 1994.
5. **Czuba R. (red.).:** Nawożenie mineralne roślin uprawnych. Wyd. Zakłady Chem., Police, 1996.
6. **Czyżyk F.:** Wpływ ścieków na skład chemiczny gleb. Zesz. Probl. Post. Nauk Roln., 418, 571-576, 1995.
7. **Hermann J.:** Wpływ dawek i rodzajów wapna tlenkowego oraz hydratyzowanego na higienizację osadów ściekowych z miejskiej oczyszczalni ścieków. III Konf. Nauk. "Kompleksowe i szczegółowe problemy inżynierii środowiska". Koszalin-Ustronie Morskie, 493-501, 1997.
8. **Hickey M. G., Kittrick J. A.:** Chemical partitioning of cadmium, copper, nickel and zinc in soils and sediments containing high levels of heavy metals. J. Environ. Qual., 13, 372-376, 1984.
9. **Jakubus M., Czekała J., Blecharczyk A.:** Wpływ wieloletniego nawożenia na frakcje mikroelementów w glebie. Zesz. Probl. Post. Nauk Roln., 434, 443-448, 1996.
10. **Kabata-Pendias A., Pendias H.:** Biogeochemia pierwiastków śladowych. PWN, Warszawa, 1993.
11. **Karczewska A.:** Formy wybranych metali w poziomach powierzchniowych i podpowierzchniowych gleb zanieczyszczonych emisjami huty miedzi. Zesz. Probl. Post. Nauk Roln., 418, 481-486, 1995.
12. **Kukurenda H.:** Wpływ zmiennych czynników środowiska na przemiany manganu glebowego i jego dostępność dla owsa. Roczn. AR Poznań, Rozprawy, 137, 1976.
13. **Mazur T., Koc J.:** Badania nad wartością nawozową osadów garbarskich. Cz. IV. Wpływ nawożenia osadami garbarskimi na zmiany chemiczne właściwości gleb. Roczn. Glebozn., 37, 1, 137-146, 1976.
14. **Mercik S., Stępień W., Kubik J.:** Wpływ wieloletniego nawożenia mineralnego i organicznego na zawartość mikroelementów w glebie. Mat. VII Symp. "Mikroelementy w rolnictwie". Wrocław, 71-75, 1992.

15.**Wasiak G.**: Wytwarzanie, właściwości i gospodarka osadami ściekowymi w Polsce na tle zachodniej Europy i USA. Sem. Nauk.-Tech. "Przyrodnicze użytkowanie osadów ściekowych. Warszawa, 11-23, 1994.
16.**Wiśniewski W., Wegner K., Gonet S.S.**: Wpływ mineralnego i organicznego nawożenia na jakość próchnicy. Roczn. Glebozn., 37, 2-3, 287-294, 1986.
17.**Wyczółkowski A.I., Baranowska M., Dąbek-Szreniawska M., Baran S.**: Kształtowanie się mikroflory w czasie kompostowania materiałów roślinnych. Symp. Mikrobiol. "Drobnoustrije a życie gleby". Kraków-Muszyna, 655-661, 1997.
18.**Zeien H., Brummer G. W.**: Chemische Extraktionen zur Bestimmung von Schwermetailbindungsformen in Boden. Mitteilgn. Dtsch. Bodenkundl. Gesellsch., 59, 1, 505-510, 1989.