

EFFECT OF VARIOUS ORGANIC FERTILISERS ON THE HEAVY METAL
FRACTIONS IN THE SOIL
Part 2. CHROMIUM AND CADMIUM

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A b s t r a c t. The subject of the paper was to determine chromium and cadmium fractions in the soils treated with tannery organic materials. Methods, characteristics of experimental materials and the tested soils were presented in the first part of the paper. After four years of investigations soil samples were collected for the assessment of the total content of chromium and cadmium and their fractions.

Results of a sequential chemical extraction confirmed literature data on the weak mobility of this metal in the soil. After application of the studied fertilisers, the share of the most mobile Cr fractions was slight. Iron oxides and residual fractions were most important for chromium accumulation.

Cadmium mobility in the soil and its easy uptake by plants is related to a considerable share of mobile forms. A large share of mobile form was noticed in the analysed soils (54.5-68.3%). Exchangeable fraction bound smaller amounts of cadmium (6.8-13.2%). Similar amounts of cadmium were accumulated in the fractions bound to manganese oxides (8.5-19.6%). Organic matter did not contribute to this element binding and the amounts of cadmium stored in this fraction were 2.3-6.6%. Only very small amount of cadmium was accumulated in the form bound with the initial minerals.

K e y w o r d s: soil, organic materials, chemical extraction, chromium, cadmium.

INTRODUCTION

Deterioration of arable lands resulting from anthropopressure is, among others, connected with an increase of heavy metals in them. The source of heavy metals are industrial wastes from mining, metallurgical, chemical, and power plants or food industry [2] often utilised by agriculture, e.g. for soil deacidification. The sources of heavy metals may be also organic wastes and industrial and municipal sewage sludge. An example of such materials may be tannery sewage sludge whose fertilising value is compared to farmyard manure, as confirmed by many papers [9,11,19,20]. The only obstacle which prevents its application in agriculture is

chromium content exceeding the suggested limit of $1000 \text{ mg Cr kg}^{-1}$ of dry mass [14]. Application of those sludges does not cause an increase in other metal contents in plants except for chromium which accumulates mainly in roots [10,17,18,21]. Tannery sludge favourably affect some soil properties, contents of carbon and nitrogen and soil reaction [12,21]. In the studies conducted so far on the tannery sludge utilisation in agriculture, only some attention was paid to the occurrence of various forms of heavy metals and their solubility related to their availability for plants. Less available metal forms are less important for the organisms living in the soil environment. Bio-availability and solubility of heavy metals depended on the metal chemical form and soil properties. Oxidation and reduction conditions related to soil moisture and reaction are very important for the activation or immobilisation of those substances [3,15,22].

The present investigations aimed at determining forms in which chromium and cadmium occur in soils. The analysis was conducted using the Zeien and Brummer's sequential chemical extraction method [29].

MATERIALS AND METHODS

Description of methods, characteristics of materials used for the experiment and detailed characteristics of the experimental soil were presented in the first part of this paper.

After four years of the experiment, Cr and Cd fractions were assayed in the medium soil samples using the Zeien and Brummer's sequential chemical extraction method [29]; the following fractions were considered:

F₁ - mobile ($1 \text{ M NH}_4\text{NO}_3$)

F₂ - exchangeable ($1 \text{ M NH}_4\text{COOCH}_3$)

F₃ - attached to manganese oxides ($1 \text{ M NH}_2\text{OH-HCl} + 1 \text{ M NH}_4\text{COOCH}_3$)

F₄ - attached to organic matter ($0.025 \text{ M NH}_4\text{-EDTA}$)

F₅ - attached to poorly crystallised iron oxides ($0.2 \text{ M ammonium oxalate}$)

F₆ - attached to fully crystallised iron oxides ($0.2 \text{ ammonium oxalate} + \text{ascorbic acid}$)

F₇ - residual ($65\% \text{ HClO}_4$).

RESULTS AND DISCUSSION

Experimental materials (sewage sludge and compost) were characterised by a considerable content of chromium which highly exceeded this element level in farmyard manure. In peat compost, the level was exceeded 18 times and in raw

sludge 17 times. Such a huge load of this metal could suggest big changes both in total chromium contents in the soil and in its distribution among individual fractions. Double peat compost and crude sludge doses caused 2 and 1.5 fold increase in the soil total chromium in relation to the control soil from the untreated plot (Table 1). Total chromium content does not allow to determine direction of changes in the soil after the application of organic materials from tannery. Other authors stated a slight mobility of chromium in sewage sludge, which allows to presume that chromium from the applied fertilisation occurs in the forms less available to plants [8,26].

The results of sequential chemical extraction according to Zeien and Brummer confirmed the assumptions. Chromium distribution among fractions did not depend on treatment, and the share of most mobile fractions was slight. The proportions of three, most mobile fractions (F₁, F₂, and F₃) were between 0.28% in the control soil and 0.60% in the soil treated with a double dose of NPK (Table 1). In the soil fertilised with raw and composted sludge, it did not exceed 0.5% of total contents. Chromium fixation by organic matter looked slightly different.

The obtained results revealed that over 1% Cr, except for the control soil (0.97%), was bound with soil organic matter. Organic matter of the soil treated with a double NPK dose, fixed the greatest amounts of chromium (2.65%) and with a double dose of manure (2.24%). Some authors reveal no dependence between the amount of humus and total chromium [27,28]. Many authors have reported that this metal is easily fixed by organic matter [1].

Chromium fixation by organic matter depends on quantitative and qualitative composition of humus compounds with which it forms metalo-organic complexes [1,24,25]. In the presented experiment, iron oxides and residual fraction played the

Table 1. Percentage distribution of chromium fractions in total Cr 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 |
| A. No fertilization | 12.51 | 0.14 | 0.05 | 0.09 | 0.97 | 11.23 | 21.22 | 66.30 |
| B. FYM I* | 11.22 | 0.15 | 0.07 | 0.11 | 1.35 | 11.63 | 19.48 | 67.22 |
| C. FYM II* | 10.31 | 0.12 | 0.01 | 0.18 | 2.25 | 13.53 | 20.80 | 62.99 |
| D. Peat compost I* | 22.09 | 0.08 | 0.10 | 0.18 | 1.59 | 18.11 | 34.46 | 45.44 |
| E. Peat compost II* | 31.04 | 0.15 | 0.08 | 0.13 | 1.45 | 17.70 | 49.13 | 31.43 |
| F. Sludge I* | 14.55 | 0.11 | 0.01 | 0.08 | 1.94 | 13.26 | 29.00 | 55.56 |
| G. Sludge II* | 18.09 | 0.20 | 0.09 | 0.15 | 1.35 | 15.56 | 32.09 | 50.64 |
| H. Mineral fertilization I* | 10.51 | 0.26 | 0.08 | 0.13 | 1.62 | 11.52 | 25.22 | 61.24 |
| I. Mineral fertilization II* | 9.02 | 0.26 | 0.21 | 0.13 | 2.65 | 12.59 | 22.59 | 61.58 |

* I - single dose, II - double dose; ** sum of fraction F₁ - F₇.

main role in chromium accumulation. Iron oxides sorptive capacity in relation to chromium depends on the soil reaction. The highest efficiency is observed in the very acid range, below pH 5.5, the fact stated by Karczewska and Spiak in their studies on the chromate sorption on iron and manganese oxides related to soil reaction [15,16]. Summary percentage of the two Cr fractions in the total contents attached to the amorphous and crystalline iron oxides ranged between 32.4% in the control soil and 66.83 % in the soil fertilised with a double dose of peat compost. While analysing the contents of those two fractions, one may notice that double doses of sludge and manure influenced an increase in the share of those fractions. The main part of chromium accumulated in the residual fraction was bound with the inner crystalline lattices of primeval minerals. It ranged between 31.43 and 67.22% of the total contents. The lowest values were detected in the soil treated with a double (31.43%) and single compost dose (45.44%). Czekała's [6] studies confirm the theory that a considerable portion of total chromium (80-90%) is fixed in permanent organic and mineral combinations. One should remember that those proportions may be shaped by various soil components, including clayey minerals, sesquioxides and soil humus.

Total cadmium contents in the soil from individual treatments did not reveal any clear differentiation and ranged between 0.513-0.673 mg kg⁻¹ of air dry mass (Table 2). In comparison to the control (untreated) soil, slightly higher Cd concentrations were observed in the soil treated with FYM and organic fertilisers. Cadmium behaviour in the soil and its distribution among the fractions revealed an opposite dependency than for chromium. High mobility of cadmium in the soil and its easy availability for plants are connected with a considerable share of mobile forms. In the analysed soil, a high proportion of mobile forms was noted, i.e. between 54.51% in the soil fertilised with a double dose of compost and 68.38% of total contents in the soil treated with a single dose of manure. Exchangeable fraction contained lower amounts of cadmium, ranging between 6.85% in the soil treated with manure (double dose) and 13.20% after the fertiliser single dose application. The fraction attached to manganese oxides accumulated slightly more cadmium (8.49-19.59%). Introducing cadmium carbonate into the soil, Chłopecka [27] stated that it considerably influenced the change in this metal distribution among individual fractions. High mobility of cadmium is also affected by this metal weak fixation by organic matter [23]. In our investigations organic matter highly contributed to this element binding, and the amounts of cadmium accumulated in this fraction ranged between 2.34 and 6.60%. However, its increased share may be seen after the application of crude sludge and NPK mineral fertilisation.

Table 2. Percentage distribution of cadmium fractions in total Cd 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 |
| A. No fertilization | 0.513 | 62.28 | 11.60 | 15.11 | 2.34 | 1.27 | 7.31 | 0.09 |
| B. FYM I* | 0.527 | 68.38 | 13.20 | 11.11 | 2.47 | 0.76 | 4.08 | 0.04 |
| C. FYM II* | 0.672 | 66.13 | 6.85 | 8.49 | 2.53 | 1.34 | 3.35 | 0.05 |
| D. Peat compost I* | 0.499 | 61.86 | 9.82 | 11.72 | 3.41 | 2.10 | 6.81 | 0.04 |
| E. Peat compost II* | 0.437 | 54.51 | 8.93 | 19.59 | 3.09 | 0.69 | 5.84 | 0.05 |
| F. Sludge I* | 0.477 | 63.61 | 13.10 | 17.40 | 6.60 | 1.26 | 7.13 | 0.04 |
| G. Sludge II* | 0.535 | 58.82 | 12.16 | 13.38 | 5.05 | 1.19 | 5.61 | 0.05 |
| H. Mineral fertilization I* | 0.459 | 65.27 | 12.20 | 15.14 | 4.79 | 2.83 | 6.21 | 0.05 |
| I. Mineral fertilization II* | 0.598 | 65.27 | 10.13 | 10.96 | 5.61 | 1.34 | 6.69 | 0.05 |

* I - single dose, II - double dose; ** sum of fraction F₁ - F₇.

Joint share of F₅ and F₆ fractions attached to iron oxides ranged from 4.69% in the soil after the application of double manure dose to 9.04% of the total soil contents after a single dose of mineral fertilisation. Very small, even trace amount of cadmium was linked with primeval minerals (F₇), which confirms the theories about high mobility of this element in soil [13].

CONCLUSIONS

1. Application of sewage sludge and its compost with peat caused an increase in the total forms of chromium, but had no influence on total contents of cadmium in soil.

2. Percentage share of chromium depended on the amount of this metal introduced with fertilisers.

3. The share in total contents of active chromium forms (F₁-F₂) and F₄ linked with organic matter, was small (1.25-3.25%). The biggest amount of chromium was detected in the fraction attached to iron oxides and to the residual fraction.

4. Cadmium was characterised by high mobility in the soil which confirms its big share (over 50%) in the mobile fraction and the trace amounts of this element bound in the residual fraction.

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