

Estimation of Bioavailability of Copper, Lead and Zinc in Municipal Solid Waste and Compost

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The influence of composting on the concentrations of copper, lead and zinc from municipal solid waste is conducted. The composition of composts obtained from municipal wastes by biothermic method DANO in Kolobrzeg was investigated. In the waste, copper occurs in the not easily available fractions. Most of the metal is bound in the organic and residual forms. While lead occurs in the available fractions and was partitioned between organic and carbonate-bound fractions. During the composting process, the major portions of lead were found in the oxide and residual fractions. Zinc was mainly associated with Fe/Mn oxides and carbonate-bound fraction. During the composting process amount of metals decreases in the exchangeable and organically bound fractions. In general, all metals concentrations increased in the final compost due to decomposition of organic matter. Metal distributions in the different chemical forms were dependent on composting age, total metal concentrations in the compost, pH, contents of organic matter and concentrations of compounds of Ca and Fe. In mature compost, amount of metals increases in the low mobile and residual fractions.

Key Words: Municipal solid waste, Compost, Bioavailability, Sequential extraction.

INTRODUCTION

The Solid Waste Management Act and other legal instruments control management of municipal solid waste in Poland¹⁻⁴. The guidelines contained therein are aimed at prevention of excessive waste generation, promotion of its recycling and utilization as well as limitation of their deposition in landfills. The directions adopted in those laws are compatible with the EU Directives.

Solid waste can be used for industrial (construction and power industries) or non-industrial purposes (shaping land surface, soil fertilization and improvement). The waste disposal can be accomplished through thermal combustion, application of physicochemical methods (oxidation, reduction, solidification and neutralization) and composting or biodegradation in soil. Composting is one of the most ecological methods used for waste disposal. The process leads to biological

decomposition of organic matter under controlled oxygen conditions. The produced compost is a product of biological activity of soil-occurring organisms. The end product is biomass featuring humus character⁵⁻¹⁰.

Whenever supplying compost made of municipal waste into soil, one must be aware that this may enrich the environment with toxic substances. One of the criteria used for compost quality assessment is the heavy metals content contributed by a given metal into the environment. However, determination of total metals content does not allow for unambiguous determination of the hazard brought by a given metal into the environment. Toxic properties of elements depend not only on their concentration but mostly on the form of their occurrence¹⁰⁻¹⁶.

This paper is an attempt to estimate the mobility of some heavy metals in solid waste and in compost made thereof.

EXPERIMENTAL

The solid waste and compost samples for tests were taken from the Municipal Waste Disposal Facility in Kolobrzeg in the years 1999–2001. The compost facility operates on the technological principle close to that applied in DANO. This is a two-stage composting. The first stage of composting is carried out in a biostabilizer, where deep biochemical transformations proceed (3–4 days); the second stage is compost ripening in heaps (4 months)⁵.

Three fractions received by way of waste screen analysis were taken for testing coarse (10×10), medium ($1 \times 1 < x < 10 \times 10$) and fine fraction ($< 1 \times 1$). Organic parts were separated from the medium fraction and put to physicochemical tests together with the fine fraction. During the year nine series of tests were carried out, namely for organic portion of municipal waste (org), fine portion of municipal waste (fi), fresh compost (fc), 1-month compost (c1), 2-month compost (c2), 3-month compost (c3), 4-month compost (c4) and 5-month compost (c5) taking into account the physicochemical composition and screen and morphological analysis for the solid waste.

The weighted mean value for waste characterizing the compost charge was used in statistical analysis. Its value originated from percentage shares of the organic and fine portions in the whole bulk of waste. Such course of action was determined by compost production method. The samples of compost were taken directly after departure from the biostabilizer and from compost heaps featuring various levels of ripening.

The following physicochemical tests that comprised determination of pH, humidity, total nitrogen (Kjeldahl method), organic matter as ignition loss, oxidizability (COD_{KMnO_4}), organic carbon, total phosphorus, nitrate III and V nitrogen contents were carried out.

The total content of metals (Cu, Zn, Pb, Fe, Ca) was determined through mineralization of samples with the mixture composed of 65% HNO_3 , 30% H_2O_2 and 75% $HClO_4$, using microwave energy and applying atomic absorption spectrometry. Concentrations of Pb, Cu, Zn were determined (by AAS) in particular fractions received in sequential extraction method¹⁷⁻¹⁹. 1 g sample was

subjected to sequential extraction in accordance with the following pattern (Table-1):

TABLE-1
ANALYTICAL PROCEDURE PATTERN

| Stage | Fraction | Procedure |
|-------|----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| I. | Exchange | 10 cm ³ CH ₃ COONH ₄ (1 M); pH = 7; room temperature; shaking time 1 h. |
| II. | Carbonate | 20 cm ³ CH ₃ COONa (1 M) acidified with CH ₃ COOH to pH = 5; shaking time 5 h; room temperature. |
| III. | Combined with Fe/Mn oxides | 20 cm ³ NH ₂ OH·HCl (0.04 M) in CH ₃ COOH (25%) (v/v), shaking time 5 h; temp. 95°C. |
| IV. | Organic | (a) 5 cm ³ HNO ₃ (0.02 M) + 5 cm ³ H ₂ O ₂ (30%); pH = 2; shaking time 2 h. (b) 5 cm ³ 30% H ₂ O ₂ ; pH = 2; shaking time 3 h; temp. 85°C. (c) 10 cm ³ CH ₃ COONH ₄ (3.2 M) in HNO ₃ (20%) (v/v); shaking time 0.5 h; room temperature. |
| V. | Residue | Microwave mineralization 5 cm ³ HNO ₃ (65%) + 1 cm ³ H ₂ O ₂ (30%) + 1 cm ³ HClO ₄ (75%). |

RESULTS AND DISCUSSION

The test results pertaining to physicochemical parameters and total contents of determined metals are shown in Tables 2 and 3.

TABLE-2
SELECTED PHYSICOCHEMICAL PARAMETERS OF MUNICIPAL
SOLID WASTE AND COMPOSTS

| Parameters | Org | fi | fc | c1 | c2 | c3 | c4 | c5 |
|-------------------------------------------|---------|--------|--------|--------|--------|--------|--------|--------|
| pH | 6.1 | 7.5 | 7.3 | 7.6 | 7.5 | 7.5 | 7.5 | 7.7 |
| Humidity (%) | 61.5 | 44.5 | 51.6 | 45.0 | 40.5 | 40.1 | 41.2 | 34.6 |
| Organic matter (%) | 71.2 | 39.3 | 55.5 | 43.9 | 41.4 | 36.5 | 34.5 | 34.6 |
| Organic carbon (%) | 31.7 | 19.3 | 26.3 | 23.0 | 19.8 | 19.6 | 16.3 | 17.8 |
| Total nitrogen (mg kg ⁻¹ dm) | 11889.7 | 6943.0 | 7749.0 | 6316.0 | 8040.0 | 7461.0 | 7581.0 | 7131.0 |
| Total phosphorus (mg kg ⁻¹ dm) | 2268.4 | 2022.2 | 2316.0 | 2174.0 | 2533.0 | 2268.0 | 2253.0 | 2389.0 |

TABLE-3
TOTAL AVERAGE METAL CONTENTS IN MUNICIPAL SOLID WASTE
AND COMPOSTS (mg kg⁻¹ dm)

| Metal | org | fi | fc | c1 | c2 | c3 | c4 | c5 |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cu | 23.89 | 45.12 | 96.96 | 115.5 | 101.8 | 119.7 | 138.6 | 135.2 |
| Pb | 40.92 | 100.5 | 211.7 | 331.0 | 263.5 | 281.3 | 316.1 | 287.1 |
| Zn | 643.6 | 767.0 | 1057 | 1194 | 1110 | 1141 | 1226 | 1094 |
| Fe | 3343 | 9483 | 10145 | 11038 | 12107 | 12682 | 13535 | 12171 |
| Ca | 22565 | 48789 | 38157 | 43183 | 42019 | 41721 | 45911 | 42860 |

From the tests carried out on municipal solid waste produced in the area of Kolobrzeg, it appears that the medium fraction makes *ca.* 60%. Organic portion thereof makes *ca.* 43% whereas small parts *ca.* 9%. High contribution of fertilizer components in the material favoured the composting process. Nevertheless, occurrence of harmful substances such as heavy metals was found in the compost obtained from the municipal solid waste. Compost varieties produced in the Waste Disposal Facility in Kolobrzeg complied, in majority of samples, with the standards set out in the new ordinance concerning admissible content of heavy metals in natural fertilizers²⁰⁻²². However, lead content in compost varieties often exceeded the limits of its application. Table-4 shows average concentration values for analyzed metals in 4-month compost, which has commercial value.

TABLE-4
COMPARISON OF AVERAGE TOTAL CONTENTS OF
METALS WITH ADMISSIBLE VALUES^{20, 21} (mg kg⁻¹ dm)

| Metal | Average total content | Admissible value |
|--------|-----------------------|------------------|
| Copper | 138.6 | 400 |
| Lead | 316.1 | 250 |
| Zinc | 1225 | 1500 |

The compost produced in Kolobrzeg failed to meet the quality standards applicable in some European Union countries²³ due to occurrence of all heavy metals examined. The source of heavy metals in compost is mostly small parts occurring in municipal solid waste. Heavy metals are cumulated in the organic-mineral fraction featuring grain size 0.005 mm whereas the organic fraction 1 mm contains *ca.* 40% of total metal concentration¹⁵. This means that only this part of the biomass should be used for composting purposes.

Copper

Copper occurred in solid waste and compost varieties mostly in the fraction combined with the organic matter²⁴ (*ca.* 60% thereof). The lowest metal concentrations, in all analyzed samples, were noted in the fraction combined with iron and manganese oxides (2–3%) and carbonates (6% in the case of waste material and 4% for compost varieties).

Percentage share of copper, in particular fractions of examined material, varied during the course of composting (Fig. 1). The highest percentage share of copper soluble forms was noted in solid waste material organic portions and in fresh compost (*ca.* 12%). As the process of compost ripening proceeded, copper content in that fraction was going down to 4%. The lowest percentage share of copper was noted for the carbonate and oxide fractions. In those fractions only 2–4% of the whole content occurred. Copper content in the form of sparingly soluble compounds varied in the analyzed samples between 35 (fc) to 22% (c1). The metal content in fraction V depended on the sample number and on the content of copper combined with organic matter (50–70%).

In case of copper, some stray results were noted; this was probably caused by occurrence of pieces of metallic copper, which were not removed during the segregation process.

Having compared the average copper concentration in the organic and fine portion of municipal solid waste, one can say that concentration of the soluble forms of copper was higher for organic waste portion (org). Copper content in the other fractions was higher for the fine waste portion (fi). pH values for organic portion of solid waste changed within the 4.7 + 7.1 range. Therefore, in slightly acid medium, copper could occur in its cationic form like Cu^{2+} , $\text{Cu}_2(\text{OH})_2^{2+}$, Cu^+ or CuOH^+ whereas in alkaline environment anionic forms like $\text{Cu}(\text{OH})_3^-$ and CuO_2^{2-} could occur²⁵. pH values for fine waste portion were much higher and remained within the 5.5–9.7 range. Therefore, in that portion of solid waste copper could occur in anionic forms. High pH values were probably caused by occurrence of mineral components and ashes where copper concentration was higher than in plant remains. It is regarded that copper in ash particles is combined mostly with iron and manganese oxides and with organic compounds²⁵.

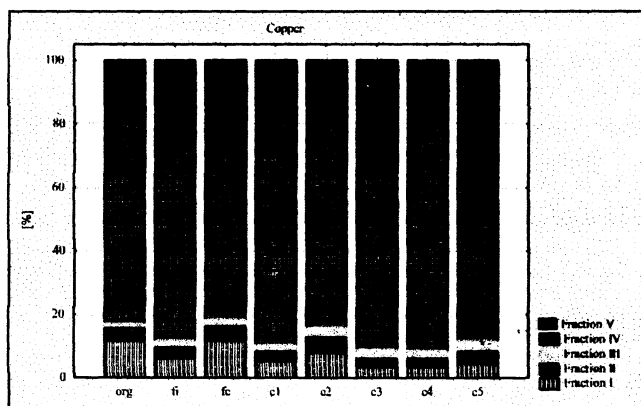


Fig. 1. Copper percentage share in particular solid waste and compost fractions

Following the variance analysis, it was established that in 2-month compost varieties the process of transformation of copper compounds occurring in the carbonate, exchange, organic matter and residue fractions was completed as no statistically significant variance differences between particular groups were noted. As far as fresh compost is concerned, the most significant change in copper content occurs in fractions IV and V. In the two most mobile fractions (exchange and carbonate) metal transformations occur during the first month of composting.

Following accomplishment of results statistical analysis, it was established that exchange copper forms in ripe compost varieties are correlated with organic matter content described by the parameter of oxidizability, organic carbon ($r_{\text{C}_{\text{org}}} = 0.61 - k_5$) and the organic matter content. Copper shows high affinity to organic compounds with which it easily makes soluble compounds²⁵. The concentration of labile forms increases with increase of organic carbon content.

In such case, copper can form complex compounds with soluble fulvic and humic acids²⁶⁻²⁸; the relationships are illustrated in Fig. 2.

Some relationships between calcium content ($r_{Ca} = 0.43 - fc$) and concentrations of soluble forms were found in the biomass used for composting and in fresh compost. Probably calcium is competitive to copper in setting bonds in a sorption complex.

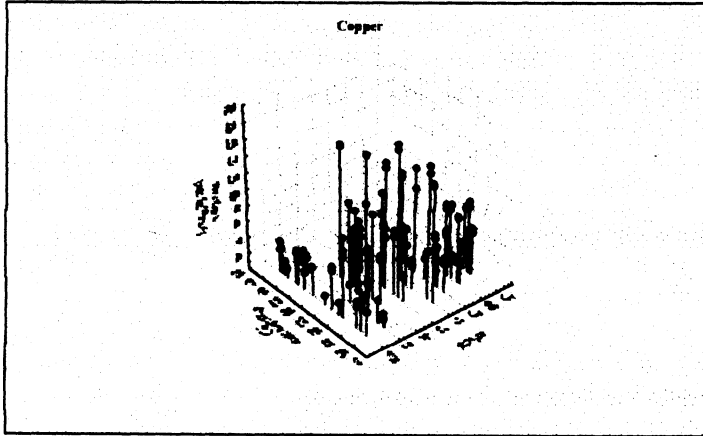


Fig. 2. Relationship between copper exchangeable form and organic carbon content and type of analyzed sample

In the case of organic fraction high negative correlations with organic carbon content and C/N ratio in compost varieties were observed (Fig. 3). Low values of C/N inform about the level of biomass ripening and humification. This confirms higher affinity of copper to humic substances having functional groups with which copper forms stable bonds²⁶. The relationship of copper concentration in organic fraction (m_0) can be described by the following regression equation:

$$m_0 = 146.93 - 3.613 \times \text{organic carbon}$$

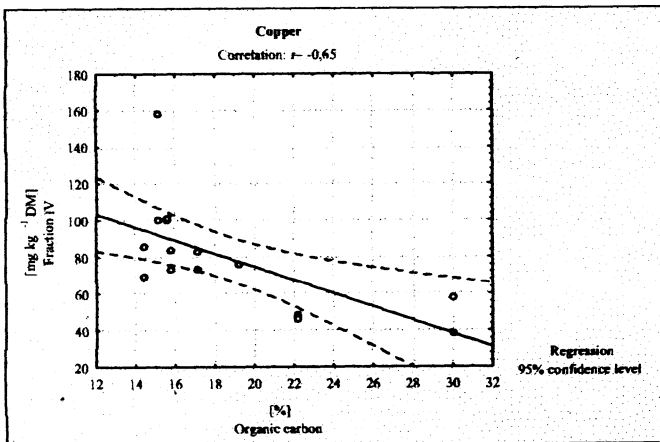


Fig. 3. Graph showing scatter of copper concentration results in organic fraction vs. organic carbon content in 5 month compost

Unfortunately, no significant correlations for fractions II and III that would describe the whole analyzed material were found. Strong correlations between total iron and calcium content and reaction occur most frequently. Previously²⁹⁻³¹, it established that free Cu^{2+} cation is coprecipitated with amphoteric iron hydroxides. This process depends on environment reaction. In alkaline reaction increased sorption of copper on iron oxides was observed whereas sorption on soluble humic compounds is more effective at lower pH values^{31, 32}. As acidity increases, within a narrow range, dissociation of carboxyl groups proceeds; therefore, copper can be combined through formation of coordinate bonds.

Lead

Percentage share of lead in the given fraction depended on type of material analysed (Fig. 4). It was associated, in the solid waste organic portion, mostly with the organic fraction where *ca.* 48% of total metal content occurred. In fresh compost the fraction made 31% whereas in ripe compost varieties it made 16–19%. The lowest percentage share in fraction combined with the residue was noted for organic portions of solid waste and for fresh compost (*ca.* 17%) whereas the highest for fine portions 41%. In ripe compost varieties it was within the range of 30–36%. In fine waste portion, the oxides made *ca.* 30% whereas in ripe compost varieties lead occurred in oxide fraction (30%) and was combined with fraction V (*ca.* 40%). During the first stage of composting lead becomes mobile because high percentage share (*ca.* 12%) of this metal was found in the exchangeable fraction whereas in the waste material (organic and fine portions) it would not exceed 4 and 1% respectively. As the compost ripens the content of exchangeable forms clearly drops and in c3, c4 and c5, it is *ca.* 16%.

During composting increase of lead percentage share in Fe/Mn oxide fraction was noted. Probably labile forms of metal get adsorbed on the oxide's surface when released during mineralization of the organic substance. In 5-month compost the percentage share made 35% of total content whereas in fresh compost this fraction made 25% and in organic parts 12%. The percentage share in the carbonate fraction practically did not change during composting (*ca.* 14–17%, only for c1 21%). The processes that proceeded in the biostabilizer caused vigorous decomposition of organic matter, which could increase the concentration of exchangeable forms of lead. In fresh compost the percentage share in the exchangeable fraction was, on average, 12% and the content of the organic fraction was reduced on average down to 30%. During compost ripening in heaps reduction of concentration of soluble lead forms was observed (*ca.* 1% for 5-month compost). Further reduction of organic fraction percentage share (19% in 5-month compost) was noted too. During the course of composting the lead content in carbonate fraction changed only slightly when compared with the content in raw waste material and fluctuated within the limits from 18% (waste mass) to *ca.* 13% in 3-month compost.

The percentage share of the examined lead fractions varied during the whole period of research work but no seasonal changes were noted. The amount of lead

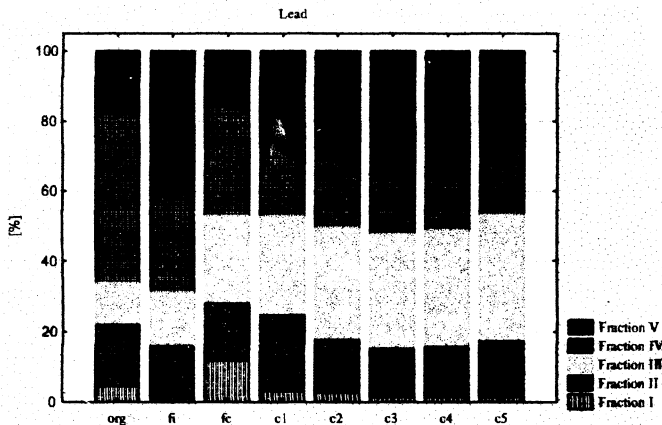


Fig. 4. Percentage share of lead in particular fractions of compost charge and compost varieties

combined with carbonates as well as iron and manganese oxides was increasing during composting. The highest scatter of results for both fractions was noted in the 5-month compost.

Lead content in all fractions of fine waste material was definitely higher than in organic portions with sole exception being fraction I. The fine portions of municipal solid waste comprised higher share of clay and ashes with which the metal is strongly bound²⁵. Lead concentration in fine portions of municipal solid waste determines its content in compost varieties.

Content of soluble lead compounds in fine portion of municipal solid waste shows high negative correlations with total nitrogen content and quantity of soluble organic compounds (oxidizability). In such a condition lead forms probably mineral connections. High pH value of solid waste suggests that lead may occur also in the form of mobile ions: PbOH^+ and $\text{Pb}(\text{CO}_3)_2^{2-}$. The organic parts of the waste material clearly feature acid reaction. Low pH values support formation of mobile lead forms: Pb^{2+} and PbHCO_3^+ and soluble organic complexes²⁵. Bivalent lead can bond with humic acids *via* carboxyl groups³².

In 5-month compost high correlation between total phosphorus and lead concentrations was noted. The correlation factor value was $r_{\text{P}_{\text{tot}}} = 0.51$. Occurrence of phosphorus (phosphates)³³ and calcium compounds causes lead retention to occur. An example of this are apatites with which it can be strongly bonded³⁴.

In ripe compost the quantity of lead occurring in the organic fraction is strongly correlated with organic carbon content (Fig. 5), therefore, with increase of the ratio that defines compost ripening level (C/N). In ripe compost, concentration of lead in fraction IV increases if and when organic carbon content increases. The lower the biomass humification level the higher the concentration of lead forming metallo-organic compounds. In effect, one can say that the concentration of the bioavailable forms of lead depends also on organic matter content^{35, 36}.

Adsorption of lead on iron and manganese oxides surface can also depend on the medium of reaction^{29, 37}. Higher concentrations of lead in fraction III were

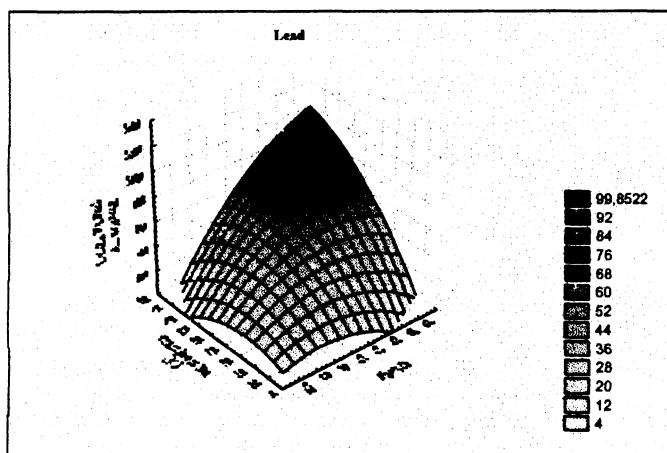


Fig. 5. Relationship between lead concentration in organic fraction and organic carbon content in tested samples

observed at higher pH values. For instance, the correlation factor for 3-month compost is $r_{pH} = 0.63$. These relationships for all analyzed samples are shown in Fig. 6. pH medium value influences in the most powerful way the content of lead bound with Fe/Mn oxides in ripe compost. No changes in lead concentration caused by reaction were observed neither in the biomass used for composting nor in fresh compost.

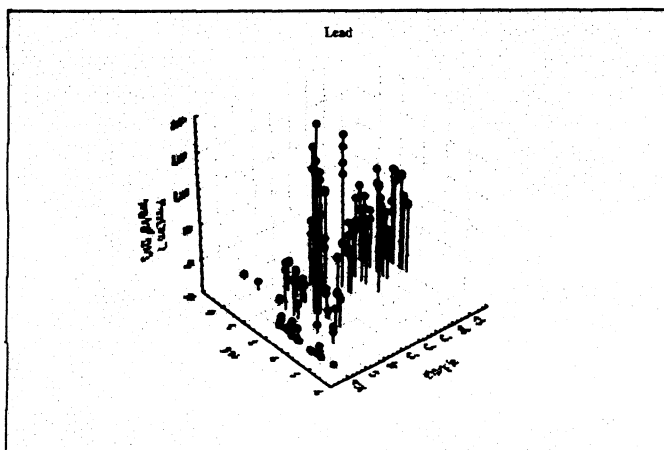


Fig. 6. Graph showing relationship between concentration of lead bound with Fe/Mn oxides and pH value in tested samples

Zinc

As one can see, zinc occurs in organic portion of municipal waste mostly in the carbonate (29.8%) and iron/manganese oxide (29%) fractions. The percentage share of zinc combined with organic matter was higher for the organic waste portion (average value 20.5%) than for fine portions (average value 13.2%). In

ripening compost varieties zinc occurred mostly in the carbonate as well as Fe/Mn oxide fractions. In fresh compost, the percentage share of zinc was distributed among three fractions: exchange (27%), carbonate (33%) and oxide (21%). The lowest zinc concentration was observed in fraction V.

The average zinc concentrations in all fractions are higher for the fine municipal solid waste part than concentration thereof in the organic portions. Zinc content in all fractions of fine waste portions influenced its quantity, in particular compost varieties. Biomass used as compost material featured high heterogeneity and showed no season-dependent qualities.

The percentage shares of particular fractions for examined material are shown in Fig. 7.

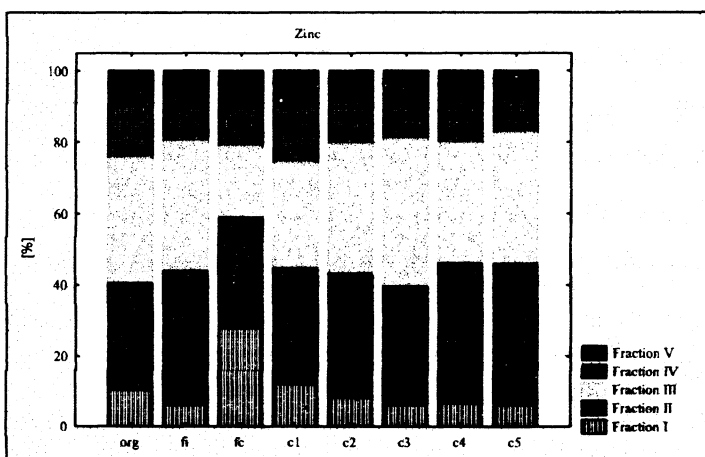


Fig. 7. Percentage share of zinc in particular fractions of the compost charge and compost varieties

During the process of composting the concentration of zinc combined with organic matter dropped down to *ca.* 10% in 5-month compost. Compared to lead and copper, zinc is weaker bound with organic matter^{15, 32}. This could have been caused by mineralization of simple organic compounds with which zinc formed metallo-organic compounds and by washing those compounds out by rainwater. The exchange fraction in the organic portion of the compost mass contained *ca.* 14% of total zinc content. Zinc could occur in the form of soluble metallo-organic compounds, which feature high mobility or as cation forms, *e.g.*, Zn^{2+} , $ZnOH^+$ and $ZnHCO_3^+$ occurring both in acid and slightly acid medium characteristic for waste organic portions²⁵.

After composting in biostabilizer, an increase of zinc concentration in exchangeable form was noted (27%: fresh compost) and then its decrease as compost ripened. Soluble zinc forms in ripe compost made *ca.* 10% of total metal content. The neutral and slightly alkaline medium in ripe compost could contribute to the formation of zinc anionic complexes²⁵, *e.g.*, $Zn(OH)_3^-$. During compost ripening small increase of zinc content in the carbonate fraction was observed. The highest percentage share of the metal was found in 5-month

compost (40%). Zinc is particularly easily bound by carbonates or adsorbed on their surface. It is quite possible that zinc soluble forms were adsorbed on carbonate surface. Similar phenomenon was observed in the case of the fraction combined with iron and manganese oxides. The lowest zinc content in this fraction was noted in fresh compost (21%) and the highest content in 3-month compost (40%). The percentage share in fraction V practically did not change in time.

Particularly, profound changes of zinc forms were observed at the first stage of composting. In 3-month compost the composting process probably stabilizes.

The statistical analysis performed showed high correlations between some physico-chemical parameters and separated fractions in examined samples. In ripe compost zinc content in fraction V was correlated with total phosphorus content ($r_{P_{tot}} = 0.76$) and depended on biomass humidification level as highly negative correlation with organic carbon $r_{C_{org}} = -0.58$ (c_5) and $r_{C_{org}} = -0.77$ for c_4 occurred.

Organic compounds that decompose during composting release zinc, which can be adsorbed on iron and manganese oxide surfaces or coprecipitated with carbonates. Such mechanism is indicated by negative correlation factors for carbonate fraction (m_C) and organic matter content ($r_{C_{org}} = -0.70$ for c_4 , which is

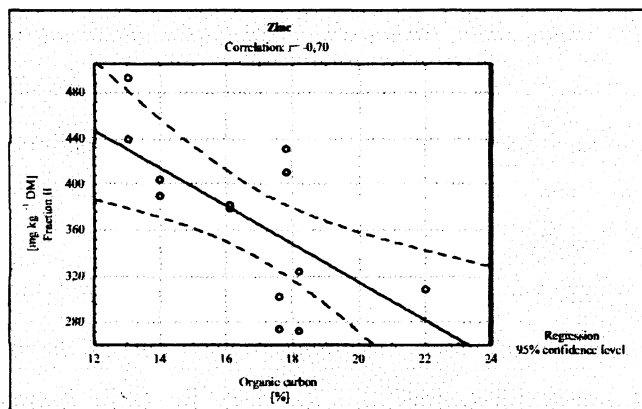


Fig. 8. Relationship between the concentration of zinc bound with carbonates and organic carbon content in 4-month compost

shown in Fig. 8) as well as for the oxide fraction (m_T) $r_{C_{org}} = -0.72$ for c_5 .

The relationships can be described by relevant linear regression equations:

$$m_C = 645.59 - 16.52 \times \text{organic carbon}$$

and

$$m_T = 539.04 - 11.03 \times \text{organic carbon}$$

A relationship with calcium content $r_{Ca} = 0.73$ for c_5 was noted also for oxide fraction (m_T). The example of existing relationships for examined parameters is shown in Fig. 9.

Calcium plays a particular role in zinc sorption on iron and manganese oxide surfaces and during their coprecipitation. The occurring mutual relationship of the parameters can be described by a linear regression equation:

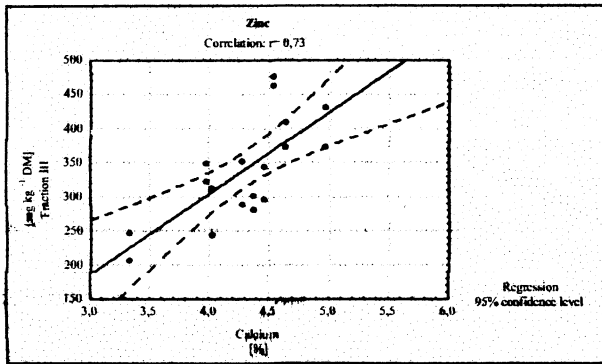


Fig. 9 Relationship between the concentration of zinc bound with Fe/Mn oxides and calcium content in 5-month compost

$$mT = -168.6 + 118.52 \times Ca$$

Correlations between concentration of total phosphorus with particular forms of zinc were noted in the analyzed material. The correlation factor value for 5-month compost is $r = 0.76$. It appears from the statistical analysis that phosphorus compounds can play a particular role in the formation of sparingly soluble zinc compounds³⁸. The relationships are shown in Fig. 10.

Zinc can also form soluble forms with organic compounds^{25, 39}. This was confirmed by high positive correlations of the metal with parameters that describe the organic matter content. As in the case of the other metals, the number of exchangeable zinc forms is decided by concentration of calcium, which can block active positions in sorption complexes in the compost samples²⁸. Addition of

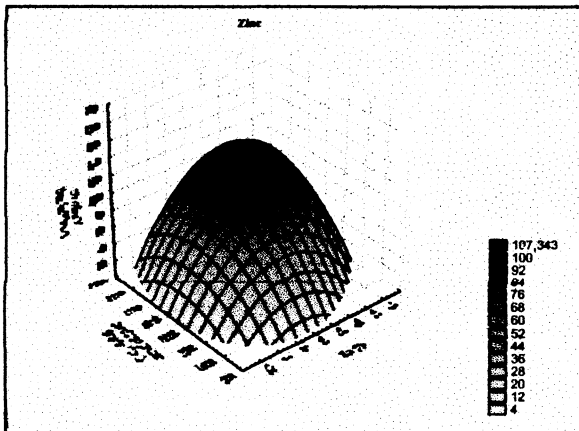


Fig. 10. Relationship between zinc concentration in fraction V and total phosphorus content in tested samples

calcium, phosphorus and sulfur compounds immobilizes the mobile forms of zinc, which are absorbed or coprecipitated on those compounds' surface²⁵.

Composting causes zinc mobility to increase. This is confirmed also by the work of Ciba and his collaborators⁴⁰. They established that metallic zinc accumulates, due to composting, mainly in the form of organic compounds and carbonates. However, zinc sulfide does not transform considerably and passes to the sulfide fraction (sequential extraction method according to Rudd), which is unavailable for the environment.

Conclusions

Biochemical transformations that occur during the first stage of composting lead to formation of metal mobile forms. Concentration of soluble forms of examined heavy metals was the highest in fresh compost. With passage of time their concentrations decreased in favour of sparingly soluble forms, hardly accessible for plants. During the first months of compost storage in heaps the occurring leachates may contain mobile forms of metals that are dangerous for the environment.

The soluble compounds of the analyzed elements, which can come from decomposition of organic matter may get to the leachate or be adsorbed by carbonates, iron and manganese oxides, humic compounds and argillaceous fraction. The leachates require special methods of detoxification to be applied.

Fractional analysis of municipal solid waste and compost samples showed differences in distribution between examined metals. Lead and copper occurred also in unavailable fractions, *i.e.*, in the fraction combined with Fe/Mn (Pb) oxides, in organic (Cu) and in V fractions. These elements form stronger bonds with organic matter than zinc. Zinc occurred mostly in the carbonate and exchange fractions. So it could be potentially dangerous for the natural environment, therefore, for human health.

In works dealing with fractioning of municipal solid waste and compost one can find various methods, differing considerably, of primary material separation into fractions. Therefore, to be able to compare the analysis results, it is essential to unify analytical procedures.

Heavy metals cumulate during composting. Their concentrations depend on initial content of organic matter and the degree of its degradation. Distribution of metals in particular fractions depends considerably on the content of calcium, which facilitates formation of sparsely soluble compounds in the water and ground environment.

Occurrence of metals in particular fractions of biomass to be composted has insignificant influence on metal forms occurrence in given fraction in compost varieties. The chemical composition of solid waste, including presence of organic and mineral matter, as well as intensity of processes that proceed in the biostabilizer and compost heaps, affects the forms of metals.

The municipal solid waste and compost is a very difficult analytical material due to its non-homogenous structure. Intensity of biochemical processes that proceed in the compost heap is strongly diversified. For this reason it is difficult

to take a representative sample for tests. Application of fractions with ever decreasing size composition, particularly in the case of organic portion of solid waste and fresh compost, could interfere with test results⁴¹. The performed analysis would pertain to a very narrow sub-fraction of the examined material, which would not reflect its real composition. There is also a problem of lack of reference materials and the intercalibration system is poorly developed.

The following conclusions appear from the tests performed on solid waste and compost varieties produced from municipal waste of Middle Pomeranian region:

- To produce compost featuring very good quality, the organic portions with grain size 1 mm should be separated from the municipal solid waste.
- The results of the analyses performed allow for determination of the degree of mobility of heavy metals contained in municipal waste and compost varieties; therefore, they can constitute an additional criterion of their quality assessment.
- Copper in ripe compost varieties occurs only in the organic matter fraction; therefore, it can be mobilized by mineralization of the matter.
- Lead in ripe compost varieties (4- and 5-month old) occurs in fractions hardly available for plants. To mobilize the metal in those fractions one should change the reduction-oxidation properties of the system and cause the organic matter to decompose. There are grounds for belief that lead occurs in compost varieties in the form of sulfides and in oxidation conditions it can be converted into sparsely soluble sulfates. It was noted that *ca.* 30% of lead is combined with fraction V. Lead compounds occurring in that fraction are practically unavailable for live organisms. The quantity of metal bioavailable for plants and environment makes *ca.* 20% of the total lead content.
- Zinc occurs in compost varieties mostly in bioavailable fractions. It is bound then with carbonates; therefore, it can be released due to change of medium pH.
- The following factors decide mostly the metal forms occurring in compost varieties: pH, organic carbon or organic matter content, occurrence of iron and calcium and compost age.
- It appears from statistical analysis that the most vigorous transformations of metal forms proceed in the biostabilizer and during the first month of compost ripening.

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