



THE INFLUENCE OF LONG-TERM FERTILIZATION WITH SLURRY, MANURE AND NPK ON THE SOIL CONTENT OF TRACE ELEMENTS

Zbigniew Mazur, Teofil Mazur

Chair of Environmental Chemistry
University of Warmia and Mazury in Olsztyn

Abstract

Long-term application of fertilizers can change the chemical composition of the soil environment. Our objective has been to determine total amounts of trace elements (Cu, Mn, Zn, Cd and Pb) in the top layer of soil after 34 years of annual applications of organic and mineral fertilizers. The first experiment was set up in 1972 on lessive soil, while the second one was started in 1973 on brown soil. The same crops were grown in both experiments. Bovine manure and slurry were applied in the first experiment, while the other one involved the application of swine manure and slurry. Slurry was applied at two different doses. One dose of slurry was applied together with manure and mineral fertilization in amounts balanced according to nitrogen. The other dose of slurry was determined so that it brought to soil the same amount of organic carbon as introduced with a manure dose. Manure and slurry were also applied in combination with phosphorus and potassium fertilizers in amounts equal half the content of these components used delivered through exclusive mineral fertilization. The total metal content was assessed using the atomic absorption spectrometry method, with prior mineralization in a 1:1 mixture of nitric and chloric acid. The application of fertilizers over many years increased the content of trace elements. The actual effect varied between the analyzed soil types, depending also on the type of fertilizer and the dose of slurry. The average content of Cu, Cd and Pb was 13.8% higher in lessive than in brown soil, while the amount Mn was lower by as much as 32.7%. Among the doses balanced with respect to nitrogen, the effect of manure caused an increase in the Mn, Zn and Ni content in lessive soil, as well as Cu and Pb in brown soil compared to the application of the slurry dose balanced with manure according to organic carbon. Mineral fertilizers did not increase the content of the analyzed metals as much as manure, with the exception of Cu and Pb in lessive soil and Ni in brown soil. Compared to manure, the application of slurry in the second dose balanced with manure using organic carbon resulted in increased concentrations of Cu and Pb in lessive soil as well as Mn, Zn, Cd and Ni in brown soil. Additional fertilization with phosphorus and potassium (PK) had various effects on the content of trace elements.

Key words: fertilization, slurry, manure, NPK, trace elements, soil.

INTRODUCTION

In addition to the contamination caused by industry or transportation, organic and mineral fertilizers can significantly alter the chemical composition of the soil environment (SU et al. 2006, JU et al. 2007, BEDNAREK et al. 2012). An indicator of these changes is the content of trace elements in soil, which is dependent on the type of fertilizer used (organic, mineral), the means and frequency of its application and the type of crops grown (HUANG, JIN 2008, SRINIVASARAO et al. 2013). When fertilizers, especially organic ones, have been applied for many years, their excessive accumulation in soil and higher uptake by plants may occur (ZENGIN, MUNZUROGLU 2005, KARIMI et al. 2013). In addition to microelements, fertilization also introduces heavy metals, which are either unnecessary or required only in small amounts in soil for the growth and development of plants; these include Pb, Cd, Cr and Hg (MORTVEDT 1996, OCIEPA et al. 2007, LUPASCU et al. 2009, GAMBUŚ, WIECZOREK 2012). Their natural content in soils does not usually impair the quality of crops. However, elevated concentrations of these elements can lead to the contamination of the agricultural environment (KABATA-PENDIAS, PIOTROWSKA 1995, *Regulation ...* 2002).

The aim of this study has been to assess the influence of fertilization with slurry, manure and NPK over a period of many years on the total content of trace elements (Mn, Zn, Cu, Cd, Ni and Pb) in the surface layer of soil.

MATERIAL AND METHODS

Soil samples from two field experiments conducted with 6 replications on randomly selected plots were used for the study. The first experiment was set up in 1972 in Balcyny (53°35'45" N, 19°51'06" E) on lessive soil, nourished with organic bovine fertilizers. The soil's arable layer consisted of sandy clay, containing 5-7% fractions under 0.002 mm in diameter (SL according to USDA). The second experiment was started a year later, in 1973, in Tomaszkowo (53°35'45" N, 19°51'06" E). It was set up on brown soil supplied with organic fertilizers from swine waste. The arable layer of the soil contained fine sand, with a 2-2.5% content of fractions under 0.002 mm in diameter (S according to USDA). The experiments compared the effects of organic (manure and slurry in two different doses) and mineral fertilizers. Beside land fertilized exclusively with organic fertilizers, plots of land fertilized naturally with the addition of mineral fertilizers (PK) were designed. Phosphorus and potassium fertilizers were applied with manure and slurry in amounts equal half of their content found in mineral fertilizers when the latter are used exclusively. The doses of slurry and manure were calculated every

year based on dry matter, organic carbon and nitrogen content, analysed directly prior to the soil enrichment. The average yearly doses of fertilizers are presented in Table 1, whereas Table 2 shows the average chemical composition of natural fertilizers. The scheme of the two experiments was composed of eight plots of land: without fertilization, dose I (dI) of slurry, dose I of slurry + PK (dI+PK), dose II (dII) of slurry, dose II of slurry + PK (dII+PK), manure, manure + PK and NPK. Slurry dose I, manure and mineral fertilizer were applied at doses balanced with nitrogen. Dose II of slurry was established so that the amount of organic carbon it introduced into the soil was equal to that in the manure dose. The following 8-year crop rotations were grown in both experiments: potato, spring barley + a mixture of red clover with grasses, red clover with grasses, winter rapeseed, winter wheat + winter rye aftercrop, corn for silage, spring barley, and winter wheat. Soil samples for analyses were taken from the top layer of the soil (0-25 cm) following the harvest of crops in 2006 (experiment I) and 2007 (experiment II). The total content of Mn, Zn, Cu, Cd, Ni and Pb was determined

Table 1

Doses of fertilizers applied in the experiments

Specification	Experiment I with bovine slurry and manure (average for 1972-2008)				Experiment II with swine slurry and manure (average for 1973-2009)			
	organic fertilizers (t ha ⁻¹ f.m.)	mineral fertilizers (kg ha ⁻¹)			organic fertilizers (t ha ⁻¹ f.m.)	mineral fertilizers (kg ha ⁻¹)		
		N	P	K		N	P	K
Manure	22.8	-	-	-	21.9	-	-	-
Slurry Dose I	40.0	-	-	-	43.1	-	-	-
Slurry Dose II	76.0	-	-	-	118.1	-	-	-
NPK	-	110	38	108	-	131	43	116

Table 2

Chemical composition of organic fertilizers (% f.m.)

Components	Experiment I (average for 1972-2008)		Experiment II (average for 1973-2009)	
	cow manure	cow slurry	swine manure	swine slurry
Dry weight	23.90	8.43	27.21	5.42
Organic carbon	8.96	3.01	9.14	1.70
Nitrogen	0.49	0.27	0.59	0.30
Phosphorus	0.15	0.11	0.28	0.19
Potassium	0.41	0.33	0.54	0.21
Magnesium	0.09	0.05	0.12	0.05

using the atomic absorption spectrometry (AAS) method after mineralization in a 1:1 mixture of nitric (V) and chloric (VII) acid. The results were subjected to statistical calculations using a Statistica 9 software package, with results of each experiment subjected to statistical analysis using the Tukey's analysis of variance. The experiments were compared with the *t*-test for independent variables, assessing differences between the average results.

RESULTS AND DISCUSSION

The two soil types differed in terms of the Cu, Zn and Mn content (Table 3). On average, lessive soil contained more copper and less manganese than brown soil but they both had similar concentrations of zinc. The total copper content in soils of the fertilized plots differed significantly from that in the

Table 3
Copper, manganese and zinc content in soils (mg kg⁻¹ d.m.)

Fertilization	Lessive soil			Brown soil		
	Cu	Mn	Zn	Cu	Mn	Zn
No fertilization	7.40	209.5	25.98	4.81	312.3	25.85
Slurry dI	10.68	247.1	29.70	5.93	367.4	28.27
Slurry dI + PK	10.14	226.7	28.94	7.72	328.6	30.78
Slurry dII	9.92	211.9	31.18	5.48	371.6	31.02
Slurry dII + PK	8.66	217.6	26.56	6.42	379.0	28.31
Manure	8.24	266.8	31.82	6.52	346.0	29.24
Manure + PK	9.56	264.6	27.19	6.80	339.7	28.88
NPK	8.22	210.6	26.77	5.50	312.0	27.66
Average	9.10 ^a	231.9 ^b	28.52 ^c	6.15 ^a	344.6 ^b	28.75 ^c
LSD _{0.05}	0.67	14.4	2.12	0.53	21.45	2.03

^{a-a}, ^{b-b} differences insignificant at $p < 0.05$, ^{c-c} differences significant at $p < 0.05$

controls. In lessive soil, the highest concentration of this element (10.68 mg kg⁻¹ d.m.) was confirmed in the plot of land supplied with slurry at dose I balanced with manure according to nitrogen, whereas the lowest one (8.22 mg kg⁻¹ d.m.) was detected in the plot subjected to mineral fertilization. The copper content in brown soil ranged from 5.48 mg kg⁻¹ d.m. in samples of soil fertilized with slurry dose II balanced with manure in terms of the amount of organic carbon, to 7.72 mg kg⁻¹ d.m. in soil fertilized with slurry dose I along with additional PK fertilization. GRÄBER et al. (2004) demonstrated that the fertilization of soil with pig manure over a period of 12 years increased the content of copper in the surface layer of soil and that the increase resulted from the content of this element in animal feed. RUTKOWSKA et al. (2009) reported that the application of mineral fertilizers and manure over a period of many years increased the Cu concentration in the soil complex. Moreover, a positive influence of the long-term application of manure and

NPK on the content of available copper forms in soil was reported by SZULC et al. (2007) and SIENKIEWICZ et al. (2009).

No significant influence of fertilization on the manganese content of either soil type was observed on NPK fertilized objects. This is corroborated by RABIKOWSKA et al. (1993), who showed that mineral NPK fertilization applied for 20 years did not have any influence on the Mn content in lessive soil. The highest manganese content in lessive soil was observed in land fertilized with manure, whereas brown soil contained the highest amounts of this element when subjected to fertilization with slurry dose II balanced with manure in terms of organic carbon. In both soils, additional PK fertilization had a negative effect on the Mn content only in the soil treated with slurry dose I. According to MERCIK et al. (2002), long-term application of manure and manure with mineral fertilizers increased the manganese content of soils. MATTIAS et al. (2002) revealed that the annual application of pig slurry could result in a very high accumulation of Mn, Cu and Zn in soils.

The concentration of zinc in lessive soil ranged from 26.56 mg kg⁻¹ d.m. in land with slurry dose II balanced with manure by the amount of organic carbon introduced into the soil, to 31.82 mg kg⁻¹ d.m. in the treatment with manure. In brown soil, the highest accumulation of this element (31.02 mg kg⁻¹ d.m.) was noted in land with slurry applied at dose II. GRÄBER et al. (2005) confirmed an increase in total zinc in the top layer of soil as a result of fertilization with swine manure. Mineral fertilization did not have a significant effect on the soil content of this element. An increase in the amount of Zn in soil was observed by OCIEPA et al. (2008) after more than a decade of applying poultry dung and swine manure. PLAZA et al. (2007) found that the application of swine slurry for a period of four years significantly increased total Mn, Zn and Cu content.

The average content of cadmium, nickel and lead was higher in lessive soil than in brown soil (Table 4). In lessive soil, cadmium ranged from 0.37 mg kg⁻¹ d.m. in the object with slurry dose II balanced with manure balanced in terms of organic carbon, to 0.48 mg kg⁻¹ d.m. in the plot fertilized with manure and additional phosphorus and potassium. In brown soil, the Cd content ranged from 0.23 mg kg⁻¹ d.m. in the control to 0.49 mg kg⁻¹ d.m. in the plot of land with slurry applied at dose II with additional PK fertilization. An increased Cd content in soil fertilized with manure is in agreement with the studies carried out by OCIEPA et al. (2008) and JU et al. (2007). This is connected with the high concentration of this element in fertilizer, amounting to 0.019-0.24 mg kg⁻¹ d.m. in Poland (OCIEPA et al. 2007).

The smallest amount of nickel in lessive soil was noted in the plot fertilized with NPK, while the soil fertilized with manure enriched with PK contained the highest amount. In brown soil, a significant divergence from the control group was found only in soil fertilized with slurry dose I balanced with manure in terms of nitrogen and with additional PK fertilization. As reported by LPIŃSKI and BEDNAREK (1997), the Ni content of soil increases

Cadmium, nickel and lead content in soils (mg kg⁻¹ d.m.)

Fertilization	Lessive soil			Brown soil		
	Cd	Ni	Pb	Cd	Ni	Pb
No fertilization	0.40	7.02	16.33	0.23	6.27	10.91
Slurry dI	0.44	7.96	16.61	0.38	6.34	12.55
Slurry dI + PK	0.44	7.82	17.87	0.27	7.13	14.60
Slurry dII	0.37	7.63	18.93	0.42	6.45	15.68
Slurry dII + PK	0.40	8.02	19.25	0.49	6.15	16.48
Manure	0.44	8.46	16.81	0.38	6.14	15.48
Manure + PK	0.48	9.31	17.62	0.42	6.22	15.24
NPK	0.38	6.68	17.07	0.24	6.37	12.17
Average	0.42 ^a	7.86 ^b	17.56 ^c	0.35 ^a	6.38 ^b	14.14 ^c
LSD _{0.05}	0.03	0.49	1.26	0.02	0.36	1.01

^{a-a} differences non-significant at $p < 0.05$, ^{b-b, c-c} differences significant at $p < 0.05$

along with an increase in the content of silt and clay fractions. Mineral fertilization was not found to significantly influence the content of cadmium and nickel in soils. ŁUKOWSKI and WIATER (2009) did not report increased concentrations of nickel when studying the effects of different mineral fertilizers.

Changes in concentrations of lead in soil induced by long-term fertilization are usually accompanied by changes in soil levels of cadmium (CLEMENTEAT et al. 2007, ATAFAR 2010). The highest Pb content in both soil types was found in land plots fertilized with dose II of slurry balanced with manure in terms of organic carbon (with and without the addition of mineral fertilizers). The reason is the high concentration of lead in organic fertilizers, which in Poland averages 4.11 mg kg⁻¹ d.m. in bovine slurry and 3.65 mg kg⁻¹ d.m. in swine slurry (OCIEPA et al. 2007).

Table 5 presents correlation coefficients between the levels of individual trace elements in lessive and brown soil. According to JIA et al. (2010), these coefficients are mainly affected by the mineralogical composition of soil and its fertility, but are also influenced by the content of trace elements in the applied fertilizers. HUANG and JIN (2008) showed that the correlation between Cu, Zn, Cd, Pb and Cr in agricultural soils depended on soil use. In lessive soil, high positive correlations were found between Mn and Cd, Mn and Ni as well as Cd and Ni, whereas in brown soil they occurred between Mn and Cd, Cd and Pb and Zn and Pb. This can be explained by the content of these elements in organic and mineral fertilizers (MAĆKOWIAK, ŻEBROWSKI 2000, OCIEPA et al. 2008a, GAMBUŚ, WIECZOREK 2012). A moderate positive correlation was verified in both soils between Cu and Zn, as well as Mn and Zn. GRÄBER et al. (2005) claimed that a significant correlation between Cu and Zn in soil was associated with the content of these elements in animal feeds. A moderate positive correlation was revealed in brown soil between Cu and Ni, Cu and Pb, and Zn and Ni, while a negative correlation was noted for Cd and Ni.

Table 5

Linear correlation coefficients between content of metals in soils

Lessive soil					
Metal	Cu	Mn	Zn	Cd	Ni
Mn	0.26*				
Zn	0.44*	0.41*			
Cd	0.34*	0.86***	0.08*		
Ni	0.38*	0.84***	0.27*	0.81**	
Pb	0.28*	-0.30*	0.05*	-0.29*	0.18*
Brown soil					
Metal	Cu	Mn	Zn	Cd	Ni
Mn	0.14*				
Zn	0.61*	0.43*			
Cd	0.24*	0.90***	0.37*		
Ni	0.51*	-0.25*	0.53*	-0.43*	
Pb	0.59*	0.66*	0.71*	0.80**	-0.03*

significant at *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

CONCLUSIONS

1. Annual fertilization with slurry, manure and mineral fertilizers continued for many years increased the total content of Cu, Mn, Zn, Cd, Ni and Pb in lessive and brown soils in relation to plots of land that had not been fertilized. The changes were more demonstrable in brown soil.

2. Among the doses of nitrogen-balanced fertilizers, manure had a more significant influence on the content of trace elements than slurry applied at a dose balanced with manure in respect of nitrogen, whereas mineral fertilization was found to have either no effect or a negative one.

3. Fertilization with phosphorus and potassium together with organic fertilizers had a significant positive effect on the content of Cu, Cd Ni and Pb in lessive soil in land plots with manure. In brown soil, such changes were noted in the content of Cu, Zn, Ni and Pb in soil to which slurry had been applied at dose I, Cu and Cd in soil with dose II of slurry, and Cd in soil treated with manure.

4. Strong positive correlations were found between the content of Mn and Cd, Mn and Ni, and Cd and Ni in lessive soil, as well as between the content of Mn and Cd, Cd and Pb, and Zn and Pb in brown soil.

REFERENCES

- ATAFAR Z., MESDAGHINIA A., NOURI J., HOMAEI M., YUNESIAN M., AHMADIMOGHADDAM M., MAHVI A. 2010. *Effect of fertilizer application on soil heavy metal concentration*. Environ Monit Assess., 160: 83-89. DOI 10.1007/s10661-008-0659-x
- BEDNAREK W., DRESLER S., TKACZYK P., HANAKA A. 2012. *Influence of liquid manure and NPK on selected sorption properties of soil*. J. Elem., 17(4): 547-557. DOI: 10.5601/jelem.2012.17.4.01
- CLEMENTE R., PAREDES C., BERNAL M.P. 2007. *A field experiment investigating the effects of olive husk and cow manure on heavy metal availability in a contaminated calcareous soil from Murcia (Spain)*. Agr. Ecosyst. Environ., 118: 319-326.
- GAMBUŚ F., WIECZOREK J. 2012. *Pollution of fertilizers with heavy metals*. Ecol. Chem. Eng., 19(4-5): 353-360.
- GRÄBER I., HANSEN J., OLESEN S., PETERSEN J., RSTERGAARD H., KROGH L. 2005. *Accumulation of copper and zinc in Danish agricultural soils in intensive pig production areas*. Dan. J. Geog., 105(2): 16-22.
- HUANG S.W., JIN J.Y. 2008. *Status of heavy metals in agricultural soils as affected by different patterns of land use*. Environ Monit Assess., 139(1-3): 317-327. DOI: 10.1007/s10661-007-9838-47-327
- JIA L.; WANG W.Y., LI Y.H., YANG L.S. 2010. *Heavy metals in soil and crops of an intensively farmed area: A case study in Yucheng City, Shandong Province, China*. Int. J. Environ. Res. Public Health, 7: 395-412. DOI: 10.3390/ijerph7020395
- JU X.T., KOU C.L., CHRISTIE P., DOU Z.X., ZHANG F.S. 2007. *Changes in the soil environment from excessive application of fertilizers and manures to two contrasting intensive cropping systems on the North China Plain*. Environ. Pollut., 145: 497-506. DOI: 10.1016/j.envpol.2006.04.017
- KABATA-PENDIAS A., PIOTROWSKA M. 1995. *Soil pollution assessment basics: Heavy metals, sulphur and PAHs*. Państwowa Inspekcja Ochrony Środowiska, pp. 41. (in Polish)
- KARIMI R., SOLHI S., SALEHI M., SOLHI M., MOLLAHOSAINI H. 2013. *Effects of Cd, Pb and Ni on growth and macronutrient contents of Vicia faba L. and Brassica arvensis L.* Intl. J. Agron. Plant Prod., 4(4): 739-744.
- LIPIŃSKI W., BEDNAREK W. 1997. *Occurrence of cadmium and nickel in soils of various granulometric composition*. Zesz. Probl. Post. Nauk Rol., 448a: 231-235. (in Polish)
- LUPASCU N., CHIRILA E., MUNTEANU M. 2009. *Heavy metal contaminants in organic fertilizers*. Ov. Univ. An. Chem., 20(2): 232-234.
- ŁUKOWSKI A., WIATER J. 2009. *The influence of mineral fertilization on heavy metal fraction content in soil. Part II. Copper and nickel*. Pol. J. Environ. Stud., 18(4): 645-650.
- MAĆKOWIAK C., ŻEBROWSKI J. 2000. *Chemical composition of manure in Poland*. Nawozy i Nawożenie, 4(5): 119-130. (in Polish)
- MATTIAS J.L., CERETTA C.A., NESI C.N., GIROTTO E., TRENTIN E.E., LOURENZI C.R., VIEIRA R.C.B. 2010. *Copper, zinc and manganese in soils of two watersheds in Santa Catarina with intensive use of pig slurry*. R. Bras. Ci. Solo, 34: 1445-1454.
- MERCİK S., LABĘTOWICZ J., STEPIEŃ W., RUTKOWSKA B., KORC M. 2002. *Availability of microelements as affected by soil reaction and fertilization in long-term field experiments*. Arch. Agron. Soil Sci., 1(1): 451-458. DOI: 10.1080/03650340215642
- MORTVEDT J. 1996. *Heavy metal contaminants in inorganic and organic fertilizers*. Fert. Res., 43: 55-61.
- OCIEPA E., PRUSZEK K., LACH J. 2008. *The changes of heavy metal content in soils under the influence of multi-year fertilization by fertilizers*. Inż. Ochr. Środ., 11(3): 281-285. (in Polish)
- OCIEPA A., PRUSZEK K., LACH J., OCIEPA E. 2008a. *Influence of long-term cultivation with manure*

- and sludge on the increase of heavy metals content in soils.* Ecol. Chem. Eng. S., 15(1): 103-109. (in Polish)
- OCIEPA E., PRUSZEK K., LACH J., OCIEPA E. 2007. *Evaluation of the usage of organic fertilizers and sewage residues as regards polluting soils by heavy metals.* Proc. ECOpole, 1(1/2): 195-199. (in Polish)
- PLAZA C., GARCÍA-GILANDA I.C., POLO A. 2005. *Effects of pig slurry application on soil chemical properties under semiarid conditions.* Agrochimica, 49(3-4): 87-92.
- RABIKOWSKA B., PISZCZ U., WILK K. 1993. *The effect of 20-year-long differentiated mineral fertilization on some properties of the loamy soil.* Zesz. Nauk. AR Kraków, 277(27): 321-332. (in Polish)
- Regulation of the Minister for the Environment of 9th Sept 2002 on Soil quality standards and land quality standards.* Dz. U. 2002, Nr 165, poz. 1359. (in Polish)
- RUTKOWSKA B., SZULC W., ŁABĘTOWICZ J. 2009. *Influence of soil fertilization on concentration of microelements in soil solutions of sandy soil.* J. Elem., 14(2): 349-355.
- SIENKIEWICZ S., WOJNOWSKA T., KRZEBIETKE S., WIERZBOWSKA J., ŻARCZYŃSKI P. 2009. *Content of available forms of some micronutrients in soil after long-term differentiated fertilization.* J. Elem., 14(4): 787-794.
- SRINIVASARAO C.H., GAYATRI S.R., VENKATESWARLU B., JAKKULA V. S., WANI S.P. KUNDU S., SAHRAWAT K.L., RAJASEKHA RAO B.K., MARIMUTHU S., GOPALA KRISHNA G. 2013. *Heavy metals concentration in soils under rainfed agro-ecosystems and their relationship with soil properties and management practices.* Int. J. Environ. Sci. Technol. 1: 1-14. DOI: 10.1007/s13762-013-0350-9
- SU Y.Z., WANG F., SUO D.R., ZHANG Z.H., DU M.W. 2006. *Long-term effect of fertilizer and manure application on soil-carbon sequestration and soil fertility under the wheat-wheat-maize cropping system in northwest China.* Nutr. Cycl. Agroecosyst. 75: 285-295. DOI: 10.1007/s10705-006-9034-x
- SZULC W., RUTKOWSKA B., BOMZE K., FELAK E. 2007. *The influence of long-term differentiated crop rotation and fertilization on content of microelements in soil.* Frag. Agronom., 24(93): 248-253.
- ZENGIN F.K., MUNZUROGLU O. 2005. *Effects of some heavy metals on content of chlorophyll, proline and some antioxidant chemicals in bean (Phaseolus vulgaris L.) seedlings.* Acta Biol. Cracov., 47(2): 157-164.