

Evaluation of the mercury content of loamy sand soil after long-term nitrogen and potassium fertilization

B. Rutkowska¹, B. Murawska², E. Spychaj-Fabisiak², Sz. Różański³,
W. Szulc¹, A. Piekut²

¹*Agricultural Chemistry Department, Faculty of Agriculture and Biology, Warsaw University of Life Sciences-SGGW, Warsaw, Poland*

²*Department of Agricultural Chemistry, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology, Bydgoszcz, Poland*

³*Department of Soil Science and Soil Protection, Faculty of Agriculture and Biotechnology, UTP University of Science and Technology, Bydgoszcz, Poland*

ABSTRACT

The study was based on soil samples taken after the long-term fertilizer experiment (1974–2014) where different doses of nitrogen and potassium were applied. The experiment was located at the Research Station of the UTP University of Science and Technology in Bydgoszcz (Poland). The long-term application of nitrogen and potassium fertilizers leads to changes in the concentration of mercury, soil acidification, reduction in total organic carbon, total nitrogen as well as affluence of available nutrients (P, K, Mg) and increased mobility of copper and zinc. The significant positive correlation between total mercury content in the soil and the content of N-NO₃, Zn, N-NH₄ and the hydrolytic acidity value were stated.

Keywords: toxic metal; pollutant; accumulation; fertility; chemical properties

In the natural environment, mercury is considered one of the most toxic metals due to its biochemical activity and variability of forms. Chemical forms, migration and binding of mercury in soils depend on many factors. Deposition of pollutants from the atmosphere and agricultural activities, including the use of pesticides and fertilizers, can often lead to mercury accumulation in soil where the content of this element exceeds 2 mg/kg of fertilizer or adjuvant (Filipek 2003, Lu et al. 2006, Kyllönen et al. 2009). Literature shows that the mercury content after the long-term application of high dose of P and K fertilizers often increases, particularly in soils which are characterized by a low mercury geochemical background (Zheng et al. 2008, Jaguś et al. 2013). The mercury content in phosphate fertilizers is 0.01–1.20 mg/kg (Kabata-Pendias and Pendias 2001), and in calcium superphosphate may reach up to 5.1 mg/kg (Zhao and Wang 2010). Moreover, there is a lack of scientific reporting on the effects

of nitrogen fertilization in the context of mercury status in soils. Therefore, it is necessary to reveal this status in agricultural soils especially in the context of the quality of crops.

The aim of this study was to answer the question of whether and to what extent the 40-year application of different doses of nitrogen and potassium fertilizers determines mercury content in the loamy sand soil. Moreover, an additional aspect of the study was to determine the relationship between the mercury content and basic fertility indicators (total nitrogen (TN), total organic carbon (TOC), pH, hydrolytic acidity (Hh), N-NH₄, N-NO₃, P, K, Mg, Cu, Zn).

MATERIAL AND METHODS

The study is based on a long-term field experiment founded in 1974 on the Albic Luvisol (IUSS 2014). The experiment is located at the Research Station

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of the UTP University of Science and Technology in Bydgoszcz (53°15'31.4"N, 17°46'40.9"E), in randomized split-plot design in three replications (Figure 1).

The first analysed factor were doses of N ($n = 3$) and the second one were K doses ($n = 4$). The average annual dose of N and K in kg/ha were as follows: N_{83} , N_{167} , N_{250} with K_0 , K_{53} , K_{105} , K_{158} . The experiment was conducted in field-feed crop rotation. Crop rotation and the level of the applied doses of nitrogen ($NH_4NO_3 - 34\% N$), potassium (KCl – 50% K) and phosphorus ($Ca(H_2PO_4)_2 - 20\% P$) are shown in Table 1.

Prior to founding the experiment in 1974 and in 2014 representative topsoil samples (composite samples of mixed cores from 0–20 cm) were collected from each investigated plot. The following parameters were determined by standard methods:

- total content of mercury in solid samples after thermal decomposition in 700°C using single-purpose atomic absorption spectrometer (mercury analyser AMA 254, Altec, Czech Republic) – validated on certified material (Table 2);
- total organic carbon content by volumetric method using 0.4 mol/L $K_2Cr_2O_7$ (Dziadowiec and Gonet 1999);
- total nitrogen – Kjeldahl method prior to mineralization in concentrated H_2SO_4 in a ratio soil:acid 1:2 (Tecator Kjeltect system 1026 Distilling Unit, Hillerød, Denmark)
- nitrate nitrogen (V) – colorimetric method using diphenyl sulfonic acid, after extraction of 1% K_2SO_4 in a ratio soil: K_2SO_4 1:5 (spectrophotometer XION 500, DR LANGE, Rhineland-Palatinate, Germany);
- ammonium nitrogen – by distillation (Tecator Kjeltect system 1026 Distilling Unit) after prior

N_1	K_2	1	N_1	K_0	13	N_3	K_2	25
N_1	K_1	2	N_1	K_1	14	N_3	K_3	26
N_1	K_0	3	N_1	K_3	15	N_3	K_0	27
N_1	K_3	4	N_1	K_2	16	N_3	K_1	28
N_2	K_0	5	N_3	K_2	17	N_2	K_3	29
N_2	K_1	6	N_3	K_0	18	N_2	K_2	30
N_2	K_2	7	N_3	K_1	19	N_2	K_1	31
N_2	K_3	8	N_3	K_3	20	N_2	K_0	32
N_3	K_3	9	N_2	K_3	21	N_1	K_2	33
N_3	K_2	10	N_2	K_0	22	N_1	K_0	34
N_3	K_1	11	N_2	K_1	23	N_1	K_1	35
N_3	K_0	12	N_2	K_2	24	N_1	K_3	36

Figure 1. Scheme of the experiment (N_1 – N_3 – nitrogen (N) dose, K_0 – K_4 – potassium (K) dose, 1–36 – plot No.)

extraction with 1% aluminium potassium sulphate (VI) in a ratio soil:sulphate 1:2;

- the content of available phosphorus (PN-R-04023, 1996) and the content of available potassium in soil according to the Egner-Riehm method (PN-R-04022, 1996) by using spectrophotometer XION 500, DR LANGE and fast sequential atomic absorption spectrometer AA240FS Varian (Santa Clara, USA);
- the content of available forms of Cu and Zn after extraction in 1 mol/L HCl, (1:10 soil:acid) on atomic absorption spectrophotometer (AA240FS Varian);
- pH – by potentiometric method after extraction in 1 mol/L KCl (1:2.5 soil:KCl), using a pH meter with glass electrode (laboratory pH meter Poland HI 4221 Mera, Warsaw, Poland);
- hydrolytic acidity (Hh) – by the Kappen's method (Ostrowska et al. 1991).

The relationship between the measured parameters was calculated statistically using the Tukey's

Table 1. Crop rotation and fertilizer doses (kg/ha)

Plant	N_1	N_2	N_3	K_0	K_1	K_2	K_3	P
Corn for silage	80	160	240	–	50	100	150	25
Winter rape	80	160	240	–	50	100	150	25
Winter wheat	50	100	150	–	33	66	100	25
Rye for green	40	80	120	–	25	50	75	25
The average annual dose	83	167	250	–	53	105	158	25

The soil pit was made for analysis of natural profile distribution of mercury (Hg), determination of Hg geochemical background and estimation of the content of the metal in surface horizon out of fertilization impact – location next to the experiment plots

Table 2. Total mercury content in certified material

Certified material	Certified value ($\mu\text{g/kg}$)	Determined value ($\mu\text{g/kg}$)	Standard deviation (%)	Number of replications
SO_4^{2-} *	30 ± 6	36.34 ± 0.43	0.8057	6

*Certificate of analysis (1995): Reference soil sample SO_4^{2-} . Canada Centre for Mineral and Energy Technology

test ($P = 0.05$) on 10.0 Statistica (Krakow, Poland). Also analysis of variance and Pearson's correlation coefficients were calculated with a confidence level of 95%.

RESULTS AND DISCUSSION

A long-term diversified fertilization, both mineral and natural, causes the change of physico-chemical properties, especially in sandy soils (Šimon and Czakó 2014, Zhang et al. 2014). This can affect the bioavailability of micro and macroelements, as well as heavy metals, and thus determine the plant nutrition and consequently the amount and quality of agricultural crops (Zimny et al. 2005, Mainville et al. 2006, Zheng et al. 2008).

It was stated that the long-term impact of high doses of nitrogen and potassium fertilizers led to acidification of sandy soil (Figure 2), changes in mercury content (Table 3) and reduction in soil fertility, and available nutrients as well as to increase in the mobility of copper and zinc (Table 4).

Following the 40-year experiment it was found that the total mercury content in the analysed soil samples ranged from 0.033–0.054 mg/kg (Table 3), and was significantly determined by different doses of applied nitrogen or potassium fertilizers and their interaction.

The total mercury content in soil samples taken from the individual plots was lower than that described by Dąbkowska-Naskręt et al. (2008) and natural for the soils of the Pomerania and Kujawy regions. It should also be noted that these do not exceed the limit value for agricultural soils (2 mg/kg), as defined in the appropriate Regulation of the Polish Minister of the Environment on soil quality standards (Regulation 2002). The average total mercury content was only 0.043 mg/kg, and was characteristic for the topsoil of the uncontaminated silty and loamy soils of Poland – from 0.01–0.90 mg/kg (Kabata-Pendias and Pendias 2001). Application of the highest doses of both nitrogen and potas-

sium fertilizers (K_1 , K_2 , K_3) significantly affected the increase of the investigated parameters. The application of higher doses of potassium (K_2 , K_3) with higher doses of nitrogen (N_2 , N_3) significantly affected the increase of mercury content in comparison to the control (K_0). The highest mercury content in the soil was found after application of the highest dose of nitrogen fertilizer (N_3 – 250 kg N/ha/year) and medium dose of potassium fertilizer (K_3 – 105 kg K/ha/year). The results are consistent with the studies of other authors, according to which the change in concentration of mercury in the soil is caused by the type of land use, including fertilizers, which determine soil fertility (Astrup et al. 1991, Lee et al. 1994, Matilainen et al. 2001, Lacerda et al. 2004, Mainville et al. 2006). Zeng et al. (2008) based on the number of long-term experiments reported increased values of mercury in soils intensively fertilized with phosphorus fertilizers. However, that concentration was mainly the effect of the geochemical background.

Profile distribution of mercury in the analysed Albic Luvisol was typical for the pedogenic process of the soil – leaching. The total content of Hg in sur-

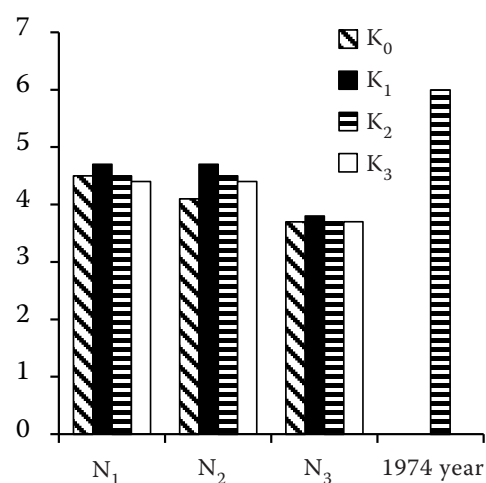


Figure 2. Changes in the pH_{KCl} values during 40 years of nitrogen and potassium fertilization

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Table 3. Total mercury content in the analysed soil samples (mg/kg)

Fertilization level	K ₀	K ₁	K ₂	K ₃
N ₁	0.047 ^{aA}	0.040 ^{bB}	0.033 ^{cC}	0.039 ^{cB}
N ₂	0.039 ^{cC}	0.042 ^{aB}	0.045 ^{bA}	0.045 ^{bA}
N ₃	0.041 ^{bC}	0.044 ^{aB}	0.054 ^{aA}	0.052 ^{aA}

^{a,b}Mean values marked with different letters in the column significantly depending on the applied nitrogen doses.^{A,B}Mean values marked with different letters in the row significantly depending on the applied potassium doses

face horizon (Ap) of control profile was 0.035 mg/kg and in parent material (C) it was 0.019 mg/kg (Table 5). In this case the concentration of the metal in surface horizon was the effect not only of the geochemical background, but also of Hg characteristics, and anthropopression (Kabata-Pendias and Pendias 2001, Rodrigues et al. 2006). The enrichment factor, calculated as a ratio of the Hg value in surface horizon and parent material (Ap/C), for the control was 1.79 and for the plot samples it ranged from 1.69–2.77. Determined concentration of mercury in surface horizons is mostly result of the limited migration of the metal. Therefore, the Hg content of surface soils is generally slowly built up, even under a low input of this metal (Roulet et al. 1998, Kabata-Pendias and Pendias 2001). Moreover, beside

the geochemical background, the most probable source of Hg is atmospheric deposition from natural and anthropogenic sources (Feng et al. 2003), but in this study the impact of fertilizers application is also possible. The values determined on experimental plots (Table 3) in comparison to the control (Ap sample, Table 5) confirm this statement.

Mercury in such fertilizers as ammonium bicarbonate, ammonia chloride, potassium chloride or urea is not detected but the concentration of the metal in ammonia sulfate (0.17 mg/kg), ammonium phosphate (0.05 mg/kg), calcium superphosphate (5.1 mg/kg) or NPK compound fertilizers (0.07–1.2 mg/kg) is much higher (Zhao and Wang 2010). In the presented experiment with different doses of nitrogen and potassium fertilizers, a constant

Table 4. Physical and chemical soil properties before the foundation of experiment (1974) and after 40 years of fertilization (2014)

Soil property	Before the experiment (1974)				After 40 years (2014)			
	range	mean	median	CV	range	mean	median	CV
TOC (g/kg)	10.0–14.5	13.0	12.8	4.89	5.40–8.04	6.60	6.66	3.48
TN (g/kg)	0.85–1.15	1.0	0.94	2.50	0.82–0.97	0.92	0.92	1.38
N-NO ₃ (mg/kg)	3.90–6.15	5.30	5.41	7.50	8.96–17.92	13.50	13.44	1.36
N-NH ₄ (mg/kg)	0.95–1.30	1.15	1.05	8.50	1.33–36.53	16.85	12.96	0.50
pH _{KCl}	5.9–6.1	6.0	5.8	–	3.7–4.8	–	–	–
Hh (mmol ₊ /kg)	13.4–15.8	14.3	14.6	2.90	21.00–39.37	30.50	30.19	3.11
P (mg/kg)	59.8–70.0	68.8	68.0	7.50	36.83–73.69	50.44	48.86	4.12
K (mg/kg)	159.0–171.2	166.7	168.3	10.25	17.14–213.05	60.67	48.97	2.42
Mg (mg/kg)	43.0–48.0	45.0	44.5	6.50	14.30–43.20	27.59	26.20	5.47
Zn (mg/kg)	4.35–5.25	4.56	4.85	7.20	5.60–12.10	8.14	7.99	6.14
Cu (mg/kg)	1.15–1.45	1.25	1.32	6.80	1.26–2.80	1.69	1.61	7.90
Hg (mg/kg)	–	0.0513*	–	–	0.0326–0.0578**	0.042	0.041	0.016

*Mercury determined by cold vapor atomic absorption technique; **mercury determined by AMA method. TOC – total organic carbon; TN – total nitrogen; Hh – hydrolitic acidity; CV – coefficient of variance

Table 5. Profile distribution of mercury (Hg)

Horizon	Ap	E	B1t	B2t	BC	C
Depth (cm)	0–28	28–41	41–73	73–113	113–132	132–150
Texture (USDA)	Loamy Sand	Loamy Sand	Sandy Loam	Sandy Loam	Sandy Loam	Loamy Sand
Hg (mg/kg)	0.035	0.016	0.022	0.021	0.023	0.019

Ap – ploughing surface horizon; E – loss of silicate clay; B1t, B2t – illuvial accumulation of silicate clay; BC – transitional horizon; C – parent material

(25 kg/ha) dose of calcium superphosphate was applied (Table 1).

Found varied values of mercury were probably related to changes of soil parameters affected by fertilization. The research results show that 40 years of intensive application of nitrogen and potassium fertilizers, on the basis of constant dose of phosphorous fertilizers, led to changes in values of acidification indicators (pH, Hh) (Table 4). The experiment led to changes in soil pH from acidic and slightly acidic category to very acidic (Table 4). Significant acidification of the soil as well as the highest concentration of mercury was observed especially in plots where the high doses of nitrogen and potassium were applied, in the ratio of N:K – 1:0.42 (Figure 2, Table 4). Higher pH values and the lowest total mercury content were found where fertilizers were applied in the ratio N:K – 1:0.63. This indicates, that determining for the acidification of the soil was not nitrogen dose but the ratio N:K in the applied fertilizers.

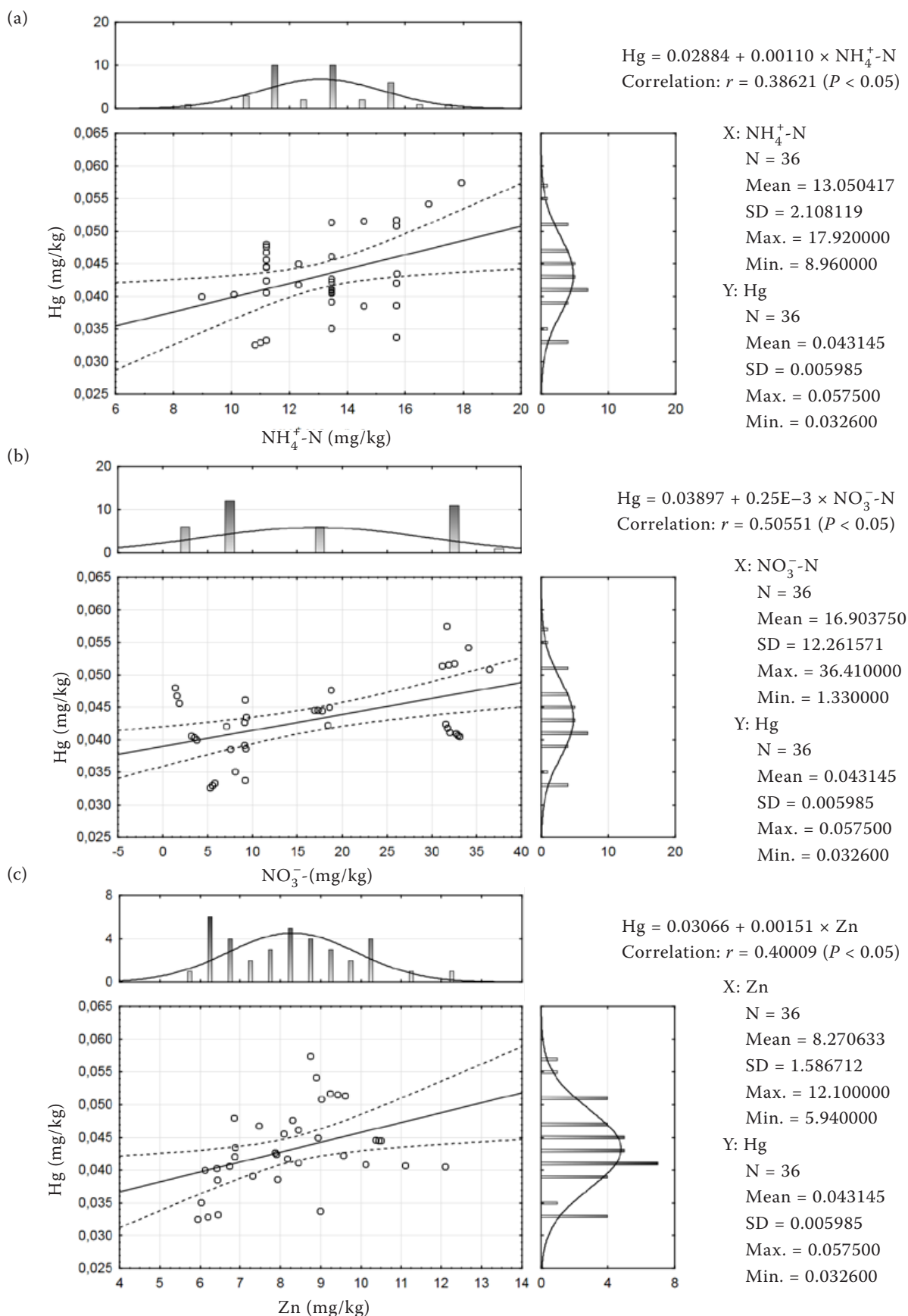
Another result of applied long-term fertilization was also a decrease in organic carbon and total nitrogen content (Table 4). It was calculated that decrease of the TOC was on average 0.24 g/kg/year. A significant reduction of TOC content, simultaneously with the increase the mercury content were found where very high doses of nitrogen (250 kg/year) and potassium (158 kg/year) were applied (Table 3). It is known that ammonium sulfate and calcium phosphate decrease the Hg uptake in roots (Kabata-Pendias and Pendias 2001), which may lead to accumulation of the metal in soil. The reduction of organic matter in the analysed soil was caused only by mineral fertilization and cultivation of plants reducing soil organic matter. Determined Hg values (not high) may still be determined by the organic matter. Strong affinity of mercury to the organic matter seems to increase with increasing soil acidity, even in sandy soils. Mercury is strongly bound

by organic compounds in a wide range between pH 3 and 12, due to the extremely high buffering capacity of humics, both in acidic and alkaline states (Kabata-Pendias and Pendias 2001). The presented results are similar to those published by other authors of which the concentration and distribution of mercury in soils is the most significantly affected by the content of organic matter (Lee et al. 1994), and less by the content of iron and aluminium oxides (Roulet et al. 1998).

The accumulation of this element depends also on microbial activity of the soil (Barkay and Wagner-Dobler 2005), and the mobility of Hg along soil profile (Roulet et al. 1998). According to these authors, mercury content is strongly correlated with physico-chemical properties of the soil. Similar results were also stated by Fernandez-Martinez et al. (2005) and Rodrigues et al. (2006).

It was shown that long-term 40-year impact of nitrogen, potassium and phosphate fertilizers generally resulted in acidification of the analysed soil (loamy sand soil), changes of the basic parameters of soil fertility (TN, TOC) and decrease of the available forms of nutrients (P, K, Mg), as well as increase in the mobility of trace elements (Cu, Zn) (Table 4). Diversified concentration of mercury in surface horizon of experimental plots was mainly the result of these changed soil properties. The significant positive correlation was stated only between the total mercury content and the content of N-NO₃, Zn, N-NH₄ and value of Hh. The correlation coefficients for these correlations were $r = 0.51$, $r = 0.40$, $r = 0.39$ and $r = 0.34$ ($P < 0.05$), respectively. For those correlations the linear regression equations were above 15% and are shown graphically in Figure 3. Determination coefficient for the relations ranged between 14–25%. As results from the data, the strongest relation was found between Hg concentrations and nitrate (V) concentrations in the soil.

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Figure 3. Correlations between mercury (Hg) content in soil and (a) $N-NH_4^+$; (b) $N-NO_3^-$; (c) zinc (Zn) content

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Corresponding author:

Prof. Beata Rutkowska, Warsaw University of Life Sciences-SGGW, Faculty of Agriculture and Biology, Agricultural Chemistry Department, Warsaw, Poland; e-mail: beata_rutkowska@sggw.pl