Vol. 18, No. 9–10

2011

Michał KOPEĆ¹ and Krzysztof GONDEK¹

EFFECT OF 40-YEAR DIVERSIFIED FERTILIZER EXPERIMENT ON CHANGES IN MERCURY CONTENT IN GRASSLAND (CZARNY POTOK)

WPŁYW 40-LETNIEGO ZRÓŻNICOWANEGO NAWOŻENIA NA ZMIANY ZAWARTOŚCI RTĘCI W ŚRODOWISKU UŻYTKU ZIELONEGO (CZARNY POTOK)

Abstract: A mountain meadow experiment localized in Czarny Potok village near Krynica (20°54′53″ E; 49°24′35″ N) and conducted since 1968 investigated the effect of diversified fertilization on the content of mercury in soil, meadow sward and applied fertilizers. Soil samples from three horizons of the limed series and the series without liming were analyzed. In the plant and soil material mercury was assessed in the AMA 254 apparatus. Relationships were sought with reference to pH, sulphur and organic carbon.

Long-term fertilization did not diversify mercury contents in the meadow sward, so the most probable agent of the differences between treatments was their botanical composition and the influence of plants on the soil physicochemical properties. Despite a high changeability of the soil pH or sulphur content in the sward, the changeability and content of mercury in the sward were not significantly diversified. Mercury contents in currently used fertilizers are low in comparison with the mercury amounts absorbed by the meadow sward. In spite of a relatively big dose of mercury which may be supplied with calcium fertilizers, no significant effect of liming on the sward mercury contents was registered.

Keywords: long-term fertilizer experiment, mercury, meadow, soil

The year 1989 was accepted in Poland as a referential year in mercury levels assessment because of the highest emission of this element to the environment reaching 39.7 mg Hg [1]. In 2000 the emission was lower by 35 % and in 2005 by 50 % in comparison with the emission in 1989. Despite these changes and dispersion of mercury in the environment, pollution with this element refers in the first place to the elements of the environment. The highest share of mercury load emitted to the atmosphere (60 %) originated from the processes of fuel use for energy generation. The second, after fuel burning, major source of this metal emission are processes of cement manufacturing, in

¹ Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 31–120 Kraków, Poland, phone: +48 12 662 43 46, fax: +48 12 662 43 41, email: m.kopec@ur.krakow.pl

which the national emission load constitutes 20 % [2]. Metallic mercury emitted into the atmosphere may cycle in it from 0.5 year to 2 years [3].

Mercury enters waters with precipitations or with groundwater and surface runoffs, however rain and snow play a special role in mercury cycling. Metal release from soil complexes may happen under favourable conditions resulting in their migration to the underground waters.

At the beginning of the eighties of the 20th century it was reported [4] that the hazard of water contamination with heavy metal compounds used in agriculture worldwide was growing particularly with reference to mercury, which was no longer used in fungicides following serious poisonings in humans and animals. Mercury, highly dispersed in water, undergoes the accumulation process, therefore considerable concentrations of this element are sometimes registered in bottom sediments of reservoirs and water-courses [5, 6].

According to Filipek [7] a potential contamination of agrosystems with mercury is relatively weak and occurs only when phosphorus fertilizers manufactured of phosphorites originating from some deposits are used. Higher contents of mercury were noted in soil even to the depth of 60 cm in the vicinity of plants manufacturing phosphorus fertilizers in Brazil [8]. According to Olendrzynski et al [2] no mercury emission is noted during phosphorus fertilizers production and their contents of this element are from 0.01 to 1.2 mg Hg \cdot kg⁻¹ [9]. Much bigger mercury amounts were registered in nitrogen fertilizers (0.3–3 mg Hg \cdot kg⁻¹) which was connected with waste utilization for these fertilizers manufacturing (waste ammonium sulphate). Currently admissible value of pollutants in organic and mineral fertilizers plant support products of mineral origin cannot exceed 2 mg Hg per 1 kg on fertilizer or plant support product weight [10]. In comparison with the year 2001, when the regulations governing fertilizers use were standardized, the criterion of mercury concentrations was significantly aggravated. At that time admissible value of pollutants in organic and organo-mineral fertilizers could not exceed 3 mg of mercury per 1 kg and in mineral fertilizers, except calcium and calcium-magnesium fertilizers, 10 mg of mercury per 1 kg of fertilizer mass [11].

In agriculture a source of mercury pollution may be sewage sludge. Sewage sludge produced in the eighties according to Strzelczuk-Ogulewicz [12] contained from 0.1 to 8.2 mg Hg \cdot kg⁻¹, but Filipek [7] reports a wide range of the contents from 0.1 to 55.0 mg Hg \cdot kg⁻¹. It evidences a greater potential of present ploughland contamination with this element in case of uncontrolled use of sewage sludge in agriculture. The permissible content in sewage sludge used for agricultural purposes is 16 mg Hg \cdot kg⁻¹ [13].

Kucharzewski et al [14] report a regional diversification of mercury content in agricultural products and its definitely bigger amounts in grasses than in cereal grain. Mercury contents in meadow sward of 48 grasslands from the Lower Silesia region were from 0.0051 to 0.0203 mg Hg \cdot kg⁻¹, but the arithmetic means from three regions fluctuated within a narrow range from 0.0119 to 0.0148 mg Hg \cdot kg⁻¹.

Regulations [15, 16] determine the permissible mercury contents in animal feeds. In feed materials mercury content cannot exceed 0.1 mg Hg \cdot kg⁻¹, except:

- feed obtained from fish, fish processing or other marine animals (to 0.5),
- calcium carbonate (to 0.3).

The aim of presented experiments was to determine the effect of cultivation measures on grasslands, mainly permanent fertilization and liming on mercury concentrations is soil and meadow sward under conditions of long-term fertilizer experiment on a mountain grassland in Czarny Potok. The conditions which formed during the 40-year experiment might have influenced mercury cycling in agrocenosis.

Material and methods

The experiment has been localized in Czarny Potok near Krynica ($20^{\circ}54'53''$ E; $49^{\circ}24'35''$ N) at the altitude of about 720 m a.s.l., at the foot of Jaworzyna Krynicka Mt. in the south-eastern massif of the Beskid Sadecki Mts., on the slope with 7° inclination and NNE exposition. The experiment was set up in 1968 on a natural mountain meadow of *Nardus stricta* L. and *Festuca rubra* L. type with a considerable share of the dicotyledonous. The soil from the experimental area was classified to acid brown soils, formed from the Magura sandstone with granulometric composition of light silt loam (with the following share of fractions: 1–0.1 mm: 40 %, 0.1–0.02 mm: 37 %, > 0.02 mm: 23 %) and characteristic three genetic horizons: AhA (0–20 cm – humus horizon), ABr (21–46 cm – browning horizon) and BbrC (47–75 cm parent rock). Details concerning the experiment were presented in a previous paper [17] and in Fig. 1.

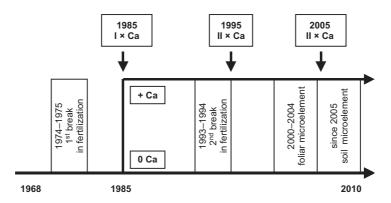


Fig. 1. Scheme of modification of treatments in the experiment

Since autumn 1985 the experiment, at the same doses of the elements, has been conducted in two series: limed and without liming. In 1995 and 2005 liming was repeated. The first and third liming were conducted using a lime dose computed on the basis of 0.5 Hh value, the second considered the total hydrolytic acidity.

In the years 1974–1975 and 1993–1994 breaks were made in mineral fertilization and the experiment was limited to determining the sward yield and its chemical composition.

The experiment, conducted in 5 replications comprises 8 fertilizer treatments (Table 1) on which unilateral nitrogen or phosphorus fertilization (90 kg N or 90 kg $P_2O_5 \cdot ha^{-1}$) against PK background (90 kg $P_2O_5 \cdot ha^{-1}$ and 150 kg $K_2O \cdot ha^{-1}$) and

nitrogen in two forms (ammonium nitrate and urea) and in two doses (90 and 180 kg $N\,\cdot\,ha^{-1})$ has been conducted.

Table 1

| Fertilising objects | Annual dose of the element in series 0 Ca and + Ca (1985, 1995, 2005) $[kg \cdot ha^{-1}]$ | | in series 0 Ca and + Ca (1985, 1995, 2005) | | d + Ca 005) | Nitrogen form | Microelements |
|------------------------|---|-------|---|---|-------------------------|---------------|---------------|
| | Р | K | Ν | | | | |
| РК | 39.24 | 124.5 | | | B; Cu, Zn, Mn, Co, Mo | | |
| PK + N | 39.24 | 124.5 | 90 | ammonium nitrate | B; Cu, Zn, Mn, Co, Mo | | |
| PK + N | 39.24 | 124.5 | 180 | ammonium nitrate | B; Cu, Zn, Mn, Co, Mo | | |
| PK + N 0 microel. | 39.24 | 124.5 | 90 | urea till 2004/ ammonium nitrate from 2005 | 0 microel. ^a | | |
| PK + N 0 microel. | 39.24 | 124.5 | 180 | urea till 2004/ ammonium nitrate from 2005 | 0 microel. | | |
| Ν | _ | _ | 90 | ammonium nitrate | B; Cu, Zn, Mn, Co, Mo | | |
| Р | 39.24 | | | | B; Cu, Zn, Mn, Co, Mo | | |
| "0" | _ | _ | _ | | B; Cu, Zn, Mn, Co, Mo | | |

Scheme of fertilization in static experiment in Czarny Potok

 a 0 microel. – (without microelements); P = 90 kg $P_2O_5,\,K$ = 150 kg $K_2O/ha;$ 0 Ca unlimed series; + Ca limed series.

In 1968–1980 phosphorus and potassium fertilizers were sown in autumn. Since 1981 the fertilizers have been sown in spring and potassium (1/2 of the dose) has been supplemented in summer after I cut. In the years 1968–1973 calcium thermophosphate (superthomasine) was used, since 1976 triple superphosphate (46 %) and since 2005 enriched superphosphate (40 %) have been applied. During the entire period of the experiment nitrogen fertilizers have been sown at two dates: 2/3 of the annual dose in spring when the vegetation started and 1/3 of the dose about two weeks after I cut. In 1994 a regenerative fertilization was applied with 10 kg Cu and 8 kg Mg \cdot ha⁻¹. In the years 2000–2004 foliar fertilizer. The fertilizer contained in 1 dm³: 23.3 g Mg, 2.3 g Fe, 2.5 g Cu, 2.7 g Mn, 1.8 g Zn, 0.15 g B and 0.1 g Mo. In the 2005–2007 period 0.5 g B per 1 h was supplied to the soil every year, whereas in the spring 2008, 5 kg Cu, Zn and Mn and 0.5 kg of Co and Mo were added per one hectare.

Vegetation period in the experimental area lasts from April to September (150–190 days). Meteorological conditions (Table 2) on the terrain where the experiment is situated indicate a considerable changeability of precipitations.

The research results presented in this paper were obtained from the soil and plant material collected in 2008 (41^{st} year of the experiment) and from analyses performed at the same time on the archival fertilizer samples. Analysis of mercury content was conducted in two replications whereas the soil and plant material were analyzed in 2008 in each replication of individual fertilizer treatments (series \cdot fertilization \cdot replication = 80 samples/1 cut or soil horizon).

Table 2

1255

| Parameters of statisti | al schedule of | precipitation and | temperatures for | period 1968-2008 |
|------------------------|----------------|-------------------|------------------|------------------|
|------------------------|----------------|-------------------|------------------|------------------|

| Parameter | Precipitat | ion [mm] | Temperature [°C] | | | |
|------------------------|-------------|-------------|------------------|-----------|--|--|
| Parameter | I–XII | IV–IX | I–XII | IV–IX | | |
| Arithmetical mean | 876.4 | 568.5 | 5.86 | 12.19 | | |
| Standard deviation | 198.7 | 138.0 | 0.87 | 0.77 | | |
| Range 25–75 % of cases | 733.2–990.0 | 461.5-658.2 | 5.35-6.30 | 11.7-12.7 | | |

Soil samples for the analysis were collected from treatments after II cut harvesting from the 0–10 cm, 10–20 cm and 20–50 cm horizons. Yields of green meadow sward mass were determined twice a year: I cut was gathered at the turn of June and July and II cut at the beginning of September.

Mercury was assessed in the plant material on AMA 254 apparatus in which it is released from the amalgamator and measured using atomic absorption at the wavelength 254 nm at the limit of quantification 0.00001 mg of mercury in the assessed sample.

Standard methods were used to determine physicochemical properties of soil: pH was assessed in water solution and 1 mol \cdot dm⁻³ KCl solution by potentiometer, organic carbon by means of the chromate method and total sulphur in plant was determined using ICP–AES method after previous sample mineralization in concentrated nitric acid and magnesium nitrate.

Results and discussion

Toxic effect of mercury is associated with this element ability to form combinations with sulfhydryl or amine groups, or with aminoacids and concerns mainly blocking their biochemical functions. Most probably a major amount of mercury absorbed by roots is bound by sulphur and does not move to plant aerial parts. However, mercury level in pollen obtained by stationary bee-yards situated in two localities near Wroclaw: agro-forest site and former military airport remained considerably higher than in the adjacent region (10–15 km north of the airport), although the airport has been closed for almost 15 years [18].

Mercury contents (Table 3) assessed in the sward from the experiment in Czarny Potok did not differ much from the values registered in other experiments [19, 20].

In 2008 mercury contents in the sward from I cut ranged, respectively from 0.0143 to 0.0236 mg Hg \cdot kg⁻¹ in the series without liming and from 0.0120 to 0.0217 mg Hg \cdot kg⁻¹ in the limed series (Table 3). Analysis of variance did not reveal any significance of differences between the series, therefore it has been not presented in the paper. Fertilization did not have any marked effect on the sward mercury concentrations, either. Differences in its content in sward from individual treatments were not unanimous, which suggests the influence of some other factors. Mercury contents in the sward from II cut in 2008 was slightly more diversified and mean content for all limed treatments was by 18.8 % higher than an average content in the sward of the treatments without liming.

Table 3

| | Fertilising objects | | | | | | | | | | |
|-------------------------|---------------------|-----------------|------------------|--------------------------------|---------------------------------|--------|--------|--------|---|--|--|
| Series/cut | РК | 90 kg N + PK | 180 kg N + PK | 90 kg N + PK; 0 microel. | 180 kg N + PK; 0 microel. | N | Р | "0" | arithmetic mean/ coefficient of variation [%] | | |
| $[mg Hg \cdot kg^{-1}]$ | | | | | | | | | | | |
| 0 Ca I cut | 0.0236 | 0.0173 | 0.0186 | 0.0166 | 0.0182 | 0.0143 | 0.0149 | 0.0146 | 0.0173/17.6 | | |
| 0 Ca II cut | 0.0169 | 0.0170 | 0.0113 | 0.0182 | 0.0163 | 0.0234 | 0.0177 | 0.0156 | 0.0170/19.6 | | |
| + Ca I cut | 0.0136 | 0.0217 | 0.0187 | 0.0164 | 0.0173 | 0.0184 | 0.0122 | 0.0120 | 0.0163/21.1 | | |
| + Ca II cut | 0.0143 | 0.0219 | 0.0221 | 0.0179 | 0.0207 | 0.0266 | 0.0242 | 0.0137 | 0.0202/22.6 | | |
| | | | | [mg S | $\cdot \text{ kg}^{-1}$] | | | | | | |
| 0 Ca I cut | 1.80 | 1.40 | 1.70 | 1.20 | 1.40 | 1.90 | 2.30 | 2.02 | 1.715/21.4 | | |
| 0 Ca II cut | 1.90 | 1.80 | 1.80 | 1.60 | 1.60 | 2.20 | 2.70 | 2.61 | 2.026/21.3 | | |
| + Ca I cut | 1.70 | 1.40 | 1.70 | 1.10 | 1.10 | 2.10 | 2.20 | 2.16 | 1.683/26.9 | | |
| + Ca II cut | 1.70 | 1.80 | 1.50 | 1.40 | 1.40 | 1.90 | 2.30 | 2.61 | 1.826/23.9 | | |
| | | | | [Mg d.r | n. \cdot ha ⁻¹] | | | | | | |
| 0 Ca I cut | 3.76 | 4.20 | 4.17 | 4.39 | 5.01 | 1.77 | 2.07 | 2.54 | 3.489/33.8 | | |
| 0 Ca II cut | 2.24 | 2.17 | 2.66 | 2.45 | 3.08 | 1.20 | 0.96 | 1.20 | 1.995/39.0 | | |
| + Ca I cut | 3.74 | 4.87 | 5.02 | 4.20 | 5.09 | 2.35 | 1.89 | 1.90 | 3.633/38.4 | | |
| + Ca II cut | 2.19 | 2.65 | 2.73 | 2.63 | 2.37 | 1.42 | 0.99 | 1.07 | 2.006/36.4 | | |
| | | | | [mg Hg | $g \cdot ha^{-1}$] | | | | | | |
| 0 Ca I cut | 88.7 | 72.7 | 77.6 | 72.9 | 91.2 | 25.3 | 30.8 | 37.1 | 62.04/43.0 | | |
| 0 Ca II cut | 37.9 | 36.9 | 30.1 | 44.6 | 50.2 | 28.1 | 17.0 | 18.7 | 32.94/35.6 | | |
| + Ca I cut | 50.9 | 105.7 | 93.9 | 68.9 | 88.1 | 43.2 | 23.1 | 22.8 | 62.08/51.6 | | |
| + Ca II cut | 31.3 | 58.0 | 60.3 | 47.1 | 49.1 | 37.8 | 24.0 | 14.7 | 40.29/40.3 | | |
| | | | | [g S - | ha^{-1}] | | | | | | |
| 0 Ca I cut | 6768 | 5880 | 7089 | 5268 | 7014 | 3363 | 4761 | 5130 | 5659/22.8 | | |
| 0 Ca II cut | 4256 | 3906 | 4788 | 3920 | 4928 | 2640 | 2592 | 3132 | 3770/23.9 | | |
| + Ca I cut | 6358 | 6818 | 8534 | 4620 | 5599 | 4935 | 4158 | 4104 | 5641/27.1 | | |
| + Ca II cut | 3723 | 4770 | 4095 | 3682 | 3318 | 2698 | 2277 | 2793 | 3419/23.9 | | |

The yield of dry mass and the content and amount of mercury and sulfur in the sward of two cuts in series with and without liming

The long-term fertilization stabilized botanical composition of the sward [21]. Botanical diversification depends mainly on soil abundance and its pH. It is difficult to seek higher mercury concentrations in the experiment at a bigger share of the dicotyledonous, which usually accumulated greater amounts of heavy metals. Presented fractional compositions (Table 4) refers to I cut sward, however characteristic is the higher content of mercury in the sward of II cut of limed series. This cut yield makes up 1/3 of the yearly yield and is characterized by a bigger share of the dicotyledonous plants on a majority of fertilizer treatments [17]. Diversified yields on the experimental

treatments caused different mercury removal. The lowest amounts of mercury taken up with the yield were noted on the treatments without fertilization and with unilateral fertilization. Differences between cuts and series concerning the amounts of absorbed mercury were noted in the year of the experiment on fertilized NPK treatments. Average quantities of mercury removed with the yield from 4 NPK fertilized treatments in I cut were, respectively 78.6 mg in the series without liming and 89.12 mg Hg \cdot kg⁻¹ d.m. in the limed series, and in II cut, respectively 40.4 and 53.6 mg Hg \cdot kg⁻¹ d.m. The values (Table 3) indicate greater amounts of mercury absorbed by the sward of limed treatments fertilized with ammonium nitrate during the whole period of experiment.

Table 4

| | Fertilising objects | | | | | | | | | |
|-----------------|--|------|------------------|-------------------------------|--------------------------------|------|------|------|--|--|
| Item | $PK = \begin{cases} 90 \text{ kg} \\ PK + N \end{cases}$ | | 180 kg PK + N | 90 kg PK + N 0 microel. | 180 kg PK + N 0 microel. | N | Р | "0" | | |
| | 0 CaO | | | | | | | | | |
| Grasses | 62.0 | 67.0 | 89.0 | 81.0 | 75.0 | 52.0 | 53.0 | 56.0 | | |
| Papilionaceae | 10.0 | 0.0 | 0.0 | 2.0 | 0.0 | 9.0 | 8.0 | 4.0 | | |
| Herbs and Weeds | 28.0 | 33.0 | 11.0 | 17.0 | 25.0 | 39.0 | 39.0 | 40.0 | | |
| | | | | + C | CaO | | | | | |
| Grasses | 92.0 | 61.0 | 60.0 | 67.0 | 77.0 | 59.0 | 44.0 | 57.0 | | |
| Papilionaceae | 5.0 | 0.0 | 0.0 | 3.0 | 1.0 | 5.0 | 5.0 | 2.0 | | |
| Herbs and Weeds | 3.0 | 39.0 | 40.0 | 30.0 | 22.0 | 36.0 | 51.0 | 41.0 | | |

Share [%] of botanical fractions in the meadow sward (2002–2003) [21]

Relatively, within the fertilizer treatments, the quantity of sulphur absorbed by Ist cut sward was not significantly diversified in comparison with the amount of mercury uptake. In case of NPK fertilized treatments the amounts of sulphur uptake fluctuated from 5268 to 7089 g S \cdot ha⁻¹ in the series without liming and from 4788 to 8534 g S \cdot ha⁻¹ in the limed series. S:Hg ratio should be emphasized, which generally was below 100 on treatments receiving NPK fertilizers and over 100 in case of simplified fertilization or the lack of it. It may evidence mercury dilution in the yield from treatments stimulated by full NPK fertilization.

The highest mercury concentrations were registered in the surface horizon (0-10 cm). In the deeper horizons mercury concentrations were decreasing. The changes were most visible between the 10-20 and 20-50 cm horizons. For both series in the 20-50 cm horizon mercury content was between 65.2 and 69.3 % of the contents from 0-10 cm horizon and between 69.2 and 77.5 % of the 10-20 cm horizon content. Statistically significant differences were also registered between the analyzed 0-10 cm and 10-20 cm horizons. No notable effect of either fertilization or liming on mercury content in soil was found.

Slightly bigger mercury contents were noted in the soil of the 10–20 cm layer of the fertilized treatments in comparison with the treatment without fertilization.

Changes of air and water conditions in soils cause mercury transformations of mercury forms. In her pot experiment Florencka [19] demonstrated a fast rate of mercury content decreasing in soils polluted with this element. Distribution of mercury compounds in soils depends mainly on oxydation-reduction conditions. Mailainen et al [22] revealed the influence of precipitations on mercury leaching from the upper soil profiles. A considerable changeability of precipitations in the experimental area (Table 2) may determine mercury forms availability to plants and this element uptake by plants. As a result of microbiological or chemical mercury methylation processes in soil, each of its form may become available to plants, but it is considered that despite vapours volatility, the process of mercury migration from soils is limited.

Mercury vapours are easily absorbed by both soil organic substance and clay minerals. The main factors increasing mercury sorption are: acidity (the best binding at pH 3–5) and organic substance, which in acid soils increases and in alkaline decreases the quantities of bound mercury [22]. In the discussed experiment the changes in mercury content between respective soil layers and treatments are conditioned by organic carbon contents and soil pH (Table 5), but most probably also by humus quality.

Other investigations conducted on the discussed experiment revealed that diversified botanical composition modifies also the runoff amount [23]. The amount of runoff in individual years or periods depended mainly on precipitations, applied fertilization and period of measurements. Therefore, larger runoffs were observed on the treatments where turf loosening occurred.

Table 5

| | | Fertilising objects | | | | | | | | | |
|-------------------------|--------|---------------------|------------------|--------------------------------|---------------------------------|--------|--------|--------|--------------------|--|--|
| Series | PK | 90 kg N + PK | 180 kg N + PK | 90 kg N + PK; 0 microel. | 180 kg N + PK; 0 microel. | N | Р | "0" | arithmetic mean | | |
| $[mg Hg \cdot kg^{-1}]$ | | | | | | | | | | | |
| 0 Ca 0–10 cm | 0.0750 | 0.0730 | 0.0740 | 0.0710 | 0.0730 | 0.0780 | 0.0750 | 0.0680 | 0.0733c* | | |
| 0 Ca 10–20 cm | 0.0681 | 0.0665 | 0.0700 | 0.0669 | 0.0702 | 0.0693 | 0.0632 | 0.0661 | 0.0690b | | |
| 0 Ca 20–50 cm | 0.0542 | 0.0455 | 0.0448 | 0.0478 | 0.0443 | 0.0480 | 0.0475 | 0.0506 | 0.0478a | | |
| + Ca 0–10 cm | 0.0770 | 0.0770 | 0.0720 | 0.0720 | 0.0720 | 0.0790 | 0.0730 | 0.0710 | 0.0741c | | |
| + Ca 10–20 cm | 0.0673 | 0.0632 | 0.0612 | 0.0698 | 0.0633 | 0.0724 | 0.0610 | 0.0721 | 0.0663b | | |
| + Ca 20–50 cm | 0.0512 | 0.0467 | 0.0504 | 0.0481 | 0.0496 | 0.0579 | 0.0532 | 0.0537 | 0.0514a | | |
| | | | | [g C · kg | g ⁻¹] | | | | | | |
| 0 Ca 0–10 cm | 24.92 | 25.12 | 22.90 | 25.14 | 23.27 | 27.44 | 25.30 | 24.00 | 24.76d | | |
| 0 Ca 10–20 cm | 10.88 | 11.91 | 10.99 | 11.45 | 10.32 | 11.25 | 11.91 | 12.06 | 11.35b | | |
| 0 Ca 20–50 cm | 7.46 | 5.31 | 7.06 | 6.66 | 7.98 | 6.86 | 6.83 | 6.70 | 6.86a | | |
| + Ca 0–10 cm | 26.62 | 26.19 | 25.45 | 26.19 | 25.40 | 26.90 | 25.69 | 28.71 | 26.39d | | |
| + Ca 10–20 cm | 13.83 | 12.99 | 13.75 | 14.43 | 13.77 | 13.86 | 13.38 | 15.84 | 13.98c | | |
| + Ca 20–50 cm | 7.53 | 8.86 | 6.28 | 6.61 | 6.02 | 7.14 | 6.83 | 6.21 | 6.94a | | |

The content of mercury and organic carbon and pH in three soil layers in series with and without liming

Table 5 contd.

1259

| | Fertilising objects | | | | | | | | | |
|---------------|---------------------|-----------------|------------------|--------------------------------|---------------------------------|------|------|------|--------------------|--|
| Series | PK | 90 kg N + PK | 180 kg N + PK | 90 kg N + PK; 0 microel. | 180 kg N + PK; 0 microel. | N | Р | "0" | arithmetic mean | |
| | pH _{KCl} | | | | | | | | | |
| 0 Ca 0–10 cm | 4.11 | 4.36 | 3.98 | 4.35 | 3.96 | 4.26 | 4.66 | 4.53 | 4.26a | |
| 0 Ca 10–20 cm | 3.94 | 4.12 | 3.92 | 4.22 | 4.06 | 3.98 | 4.35 | 4.35 | 4.12a | |
| 0 Ca 20–50 cm | 5.33 | 5.76 | 5.28 | 5.89 | 5.22 | 5.19 | 5.87 | 5.48 | 5.50d | |
| + Ca 0–10 cm | 5.45 | 5.58 | 5.07 | 5.42 | 5.29 | 5.15 | 4.42 | 5.29 | 5.34c | |
| + Ca 10–20 cm | 4.90 | 4.84 | 5.01 | 5.16 | 5.00 | 4.94 | 4.99 | 5.17 | 4.49b | |
| + Ca 20–50 cm | 5.53 | 5.64 | 5.92 | 6.07 | 5.70 | 5.81 | 5.78 | 5.82 | 5.78e | |

* Variance analysis according to Fishera p < 0.05.

Mazurek and Wieczorek [20] proved that lower content of mercury in brown soil occurs at higher hydrolytic acidity, bigger organic carbon content, CEC (*Cation-Exchange-Capacity*) and contents of < 0.02 mm fraction. Some of these parameters were confirmed by Rodrigues et al [3] based on 624 soil samples from northern Spain.

Mercury contents were analyzed in archival samples of fertilizers applied in the discussed experiment.

Among the analyzed fertilizers the highest content of mercury (Table 6), which fell within the limits stated by Filipek [7], was assessed in phosphorus fertilizers. Mercury contents assessed in potassium salts and nitrogen fertilizers were lower than quoted by Filipek [7].

Table 6

Range of mercury content [mg Hg \cdot kg⁻¹] in applied fertilizers in 1970–2008 and arithmetic mean of the element amount introduced with fertilizers on 1 ha

| Item | Number of investigated fertilizers | Range $[mg \cdot kg^{-1}]$ | Mean $[mg \cdot kg^{-1}]$ | Estimated amount of Hg introduced with fertilizers yearly $[mg \cdot ha^{-1}]$ |
|-----------------------------|--|----------------------------|---------------------------|---|
| Triple superphosphate | 5 | 0.0118-0.0599 | 0.0333 | 6.456 |
| Calcium thermophosphate | 1 | | 0.0166 | 5.976 |
| Ammonium nitrate | 6 | 0.0039-0.0191 | 0.0104 | 2.753/5.506 ^a |
| Urea | 2 | 0.0029-0.0030 | 0.0029 | 0.567/1.134 |
| Potassium salt ^b | 11 | 0.0075 - 0.0407 | 0.0162 | 4.860 |
| Calcium fertilizer | 2 | 0.0116-0.0189 | 0.0153 | 76.5–160.6 ^c |

^a Dose of 90 kg N /180 kg N \cdot ha⁻¹; ^b with a different K₂O content; ^c the range depends on different soil acidification on particular objects.

Because of calcium fertilizer doses, the biggest amounts of mercury supplied to the soil with these fertilizers, depending on the acidity they fluctuated from 76.5 to 160.6 mg

 $Hg \cdot ha^{-1}$. Estimated quantity of mercury absorbed by the meadow sward per hectare (Table 3) is significantly smaller than the amount of mercury supplied to the soil with nitrogen, phosphorus or potassium fertilization.

Conclusions

Long-term fertilization did not diversify mercury contents in meadow sward and the most likely factor of changes in the contents between treatments was their botanical composition and plant influence on soil physicochemical properties.

In spite of considerable changeability of soil pH or sulphur contents in the sward, changeability and contents of mercury in the sward were not significantly diversified.

Mercury contents in currently used fertilizers are small in comparison with mercury amount taken up by the meadow sward.

Despite a relatively big dose of mercury which may be supplied with calcium fertilizers, no marked effect of liming on mercury contents in the sward was registered.

References

- [1] Krajowa strategia ograniczenia emisji metali ciężkich. Ministerstwo Środowiska, Warszawa 2002, 28 p.
- [2] Olendrzyński K., Dębski B., Skośniewicz J., Kargulewicz I., Cieślińska J., Olecka A., Kania K., Kanafa M., Fudała J., Hławiczka S. and Cenowski M.: Inwentaryzacja emisji do powietrza SO₂, NO₂, NH₃, CO, pyłów, metali ciężkich, NMLZO i TZO w Polsce za rok 2005. Wyd. Instytut Ochrony Środowiska, Warszawa 2007, 79 p.
- [3] Rodrigez Martin J.A., Garbonel Martin G., Lopez Arias M. and Grau Corbi J.M.: Spanish J. Agric. Res. 2009, 7(1), 107–118.
- [4] Florczyk H., Gołowin S.: Ochr. Środow. 1980, 1, 12-17.
- [5] Boszke L., Kowalski A., Głosińska G., Szarek R. and Siepak J.: Polish J. Environ. Stud. 2003, 12(1), 5–13.
- [6] Boszke L. and Kowalski A.: Oceanol. Hydrobiol. Stud. 2007, XXXVI(3), 79-99.
- [7] Filipek T.: Chemik 2003, 11, 334-352.
- [8] Mirlean N., Baisch P., Machado I. and Shumilin E.: Bull. Environ. Contam. Toxicol. 2008, 81, 305–308.
- [9] Kabata-Pendias A. and Pendias H.: Biogeochemia pierwiastków śladowych, Wyd. Nauk. PWN Warszawa 1999, 400 p.
- [10] Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi w sprawie wykonania niektórych przepisów ustawy o nawozach i nawożeniu. DzU 2008, nr 119, poz. 765.
- [11] Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi w sprawie wykonania niektórych przepisów ustawy o nawozach i nawożeniu. DzU 2001, nr 60, poz. 615.
- [12] Strzelczuk-Ogulewicz H.: Ochr. Środow. 1980, 2, 48-50.
- [13] Rozporządzenie Ministra Środowiska w sprawie komunalnych osadów ściekowych. DzU 2010, nr 137, poz. 924.
- [14] Kucharzewski A., Nowak L. and Szymańska-Pulikowska A.: Acta Sci. Polon., Cirumiectus 2002, 1–2(1–2), 151–155.
- [15] Dyrektywa Komisji 2010/6/UE z dnia 9 lutego 2010 r. L37/29.
- [16] Rozporządzenie Ministra Rolnictwa i Rozwoju Wsi w sprawie dopuszczalnych zawartości substancji niepożądanych w paszach. DzU 2007, nr 20, poz. 119.
- [17] Kopeć M.: Zesz. Nauk. AR w Krakowie, 2000, ser. Rozpr, 267, p. 1-84.
- [18] Roman A.: [in:] Materiały XIII Kongresu PTNW "Od nauki do praktyki", Uniwer. Warmińsko-Mazurski w Olsztynie 2008, p. 18–19.
- [19] Florencka N.: Inż. Środow. 2004, 9(1), 93-99.
- [20] Mazurek R. and Wieczorek R.: Ecol. Chem. Eng. A 2007, 14(5-6), 497-503.
- [21] Kopeć M. and Szewczyk W.: Annales UMCS, E Agric. 61, 175-188.

1261

[22] Matilainen T., Verta M., Korhonen K., Uusi-Rauva A. and Niemi M.: Water Air Soil Pollut. 2001, 125, 105–119.

[23] Mazur K., Kopeć M. and Noworolnik A.: Zesz. Probl. Post. Nauk Roln. 2002, 482, 365-374.

WPŁYW 40-LETNIEGO ZRÓŻNICOWANEGO NAWOŻENIA NA ZMIANY ZAWARTOŚCI RTĘCI W ŚRODOWISKU UŻYTKU ZIELONEGO (CZARNY POTOK)

Katedra Chemii Rolnej i Środowiskowej Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: W górskim doświadczeniu łąkowym zlokalizowanym w Czarnym Potoku koło Krynicy (20°54′53″ E; 49°24′35″ N) prowadzonym od 1968 r. badano wpływ zróżnicowanego nawożenia na zawartość rtęci w glebie, runi łąkowej i stosowanych nawozach. Analizowano próbki glebowe z trzech poziomów 0–10 cm, 10–20 cm i 20–50 cm z serii wapnowanej i bez wapnowania. Rtęć w materiale roślinnym i glebowym oznaczono za pomocą aparatu AMA 254. Poszukiwano zależności w odniesieniu do pH, siarki i węgla organicznego.

Długotrwałe nawożenie nie zróżnicowało zawartości rtęci w runi łąkowej, a najbardziej prawdopodobnym czynnikiem różnic międzyobiektowych w zawartości był ich skład botaniczny i wpływ roślin na właściwości fizykochemiczne gleby. Pomimo dużej zmienności odczynu gleby czy zawartości siarki w runi, zmienność i zawartość rtęci w runi nie były znacząco zróżnicowane. Zawartość rtęci w obecnie stosowanych nawozach jest mała w porównaniu do ilości pobieranej rtęci przez ruń łąkową. Mimo względnie dużej dawki rtęci, która może być wprowadzona z nawozami wapniowymi, nie stwierdzono znacznego wpływu wapnowania na zawartość rtęci w runi.

Słowa kluczowe: długotrwałe doświadczenie nawozowe, rtęć, ruń, gleba