

## MODIFIED WALLSCHLÄGER SEQUENTIAL EXTRACTION AS A TOOL FOR EVALUATING THE MOBILITY OF MERCURY

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**Abstract:** The presented studies were focused on evaluating the utility of one of sequential extraction methods for evaluating the bioavailability of mercury in soils polluted by this element. Soil samples collected from horizons 0–20 cm and 20–80 cm were subject to analysis of the basic physical and chemical properties of soils. Moreover, the total content of mercury was determined and sequential extraction of mercury was conducted using a modified five-stage Wallischläger method.

The analyses show that the studied soils are characterized by a variable mercury content, the highest in the surface soil horizons. Sequential extraction of mercury in the analyzed soils has indicated that the highest percentage content in the total content had mercury linked with sulphides. A high content of mercury linked with organic matter was also noted. The content of bioavailable mercury did not exceed 1.5% of the total content.

### INTRODUCTION

Mercury is an element that is widely dispersed in the natural environment and because of its toxic properties it is essential to analyse its presence in various components of the environment. Increased mercury content in the environment unfavourably influences the biological properties of soil and has a toxic effect on plants.

Total concentrations of mercury in the soils depend upon the amounts present in the parent rocks from which the soils form as well as from atmospheric input, of both natural and human-made origin. The main source of mercury in soil is the mercury deposition from atmospheric air. Releasing the mercury into the atmosphere takes place mostly during coal combustion, as well as during other industrial processes, such as chlorine production by mercury method or cement production. The current estimated level of mercury emission from all sources in Poland makes ca. 15 Mg/year and has decreased since 1996 [4]. Although almost all industrial uses of mercury have been considerably reduced, the specific physical-chemical properties of mercury species make them stable and persistent in the environment.

However, determination of the total content of mercury does not supply complete information on the toxicity of this element, its bioavailability and potential migration in

the environment. Quantifying the geochemical phases of this element associated with soil is an important step in predicting the ultimate fate, bioavailability, and toxicity of mercury. These aspects can be resolved after distinguishing and determination of various forms of mercury during sequential extraction. Specific activity of mercury in the natural environment resulting from its unique physical and chemical properties cause that it is not possible to distinguish its forms using popular techniques of sequential extraction. Due to this fact, procedures of mercury sequential extraction are being improved recently worldwide. So far, in Poland, most of research studies have been conducted mainly to identify the total mercury contamination. However, no numerous has been an attempt to determine the available fraction by analysis of the chemical species of mercury present in contaminated soils.

The presented studies are focused on determining the mobility of mercury using modified Wallschläger sequential extraction in soils polluted by this element due to incorrect waste management.

## MATERIAL AND METHODS

The study material comprised soil samples collected from the area around a factory producing thermometers, aerometers etc. located in the vicinity of Warsaw, characterized by considerable mercury pollution despite reclamation works. The study terrain is located on the area of pine forest and is composed of Quaternary deposits representing podzol soils made of loose sands and gravels of glaciofluvial origin. The first aquifer horizon occurs at the depth of 1.5–3.5 m, depending on the precipitation and soil retention. The sample sites are presented in Figure 1.

Soil samples were collected from the surface (0–20 cm) and deeper horizons (20–80 cm). The samples were air-dried in room temperature, ground in a mortar and sieved through mesh size of 1 mm. The following properties were determined: pH in water and in 1 M KCl using the potentiometer method, organic carbon content using a TOC analyzer and total mercury content using the AMA-254 mercury analyzer. The content of the particular mercury forms was determined using sequential extraction worked out by Wallschläger and cooperates, comprising five stages [13]. Mercury sequential extraction method was chosen on the basis of our earlier studies [1].

In these studies there were used three sequential extraction method based on the methods of Hann *et al.* [9], Lechler *et al.* [10] and Wallschläger. However, only the latter method gave the greatest recoveries compared to a reference material (NIST Soil Montana 2711). The selected procedure, although operationally defined, also gave detailed information about the availability and mobility of mercury in the soil samples and could be easy applied with the available infrastructure in a standard trace metals laboratory.

The first stage is the extraction of the mercury fraction soluble in water, followed by extraction using an acid solution (0.01 M HNO<sub>3</sub>) in order to determine the poorly bound mercury complexes and/or partial dissolution of hydroxides and oxides of iron and manganese. The following two stages are focused on determining mercury linked with organic matter after extraction with an alkaline solution (1 M KOH) and determination of mercury linked with sulphides after extraction with a Na<sub>2</sub>S solution. The last stage determines mercury fractions stably linked with inorganic part of soil. In

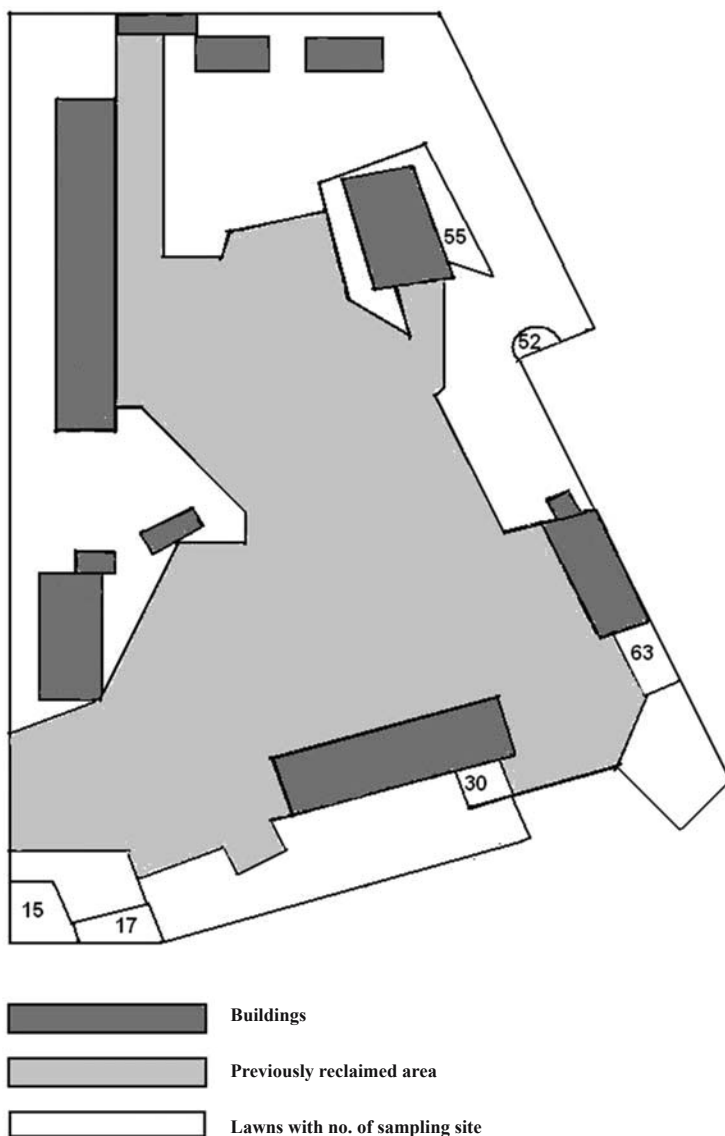


Fig. 1. Scheme of sample location

the experiment presented herein this procedure was modified. Instead of using  $\text{Na}_2\text{S}$ , the solution of  $\text{HCl}/\text{HNO}_3/\text{H}_2\text{O}$  (1:6:7, v:v:v) was applied in the fourth stage; this solution is successfully applied in determining forms of mercury linked with sulphides [5, 8]. Detailed conditions of the extraction are presented in Table 1. The content of mercury in particular fractions was determined, similarly as the total content using the AMA-254 mercury analyzer.

Table 1. Conditions of the modified Wallschläger sequential extraction

No.	Fraction	Extraction reagent		time	temperature
		Applied in the original method	Applied herein		
1.	Mercury soluble in water (F1)	Deionized water	Deionized water	24 h	room
2.	Poorly bound mercury complexes (F2)	0.01 M HNO <sub>3</sub> (pH=2)	0.01 M HNO <sub>3</sub> (pH=2)	24 h	room
3.	Mercury bound with organic matter (F3)	1 M KOH	1 M KOH	24 h	room
4.	Mercury bound with sulphides (F4)	Na <sub>2</sub> S	HCl/HNO <sub>3</sub> /H <sub>2</sub> O (1:6:7, v:v:v)	40 min	95°C
5.	Residual mercury (F5)	HNO <sub>3</sub>	HNO <sub>3</sub> /HCl (3:1, v:v)	1 h	85°C

## RESULTS AND DISCUSSION

The selected physical and chemical properties of the analyzed soils are presented in Table 2. Reaction measured in aqueous solutions was in the range of 4.8–7.9 and in 1M KCl it was within 4.0–7.9. The soils were also characterized by slight variability in the total organic carbon content, which varied within 0.11–3.43%. The highest content of organic matter was noted in samples from the surface horizons (0–20 cm).

Based on the studies it was observed that the analyzed soils show considerable variability with regard to the mercury content. The total content of mercury in the surface horizons (0–20 cm) was within 34.2–252 mg·kg<sup>-1</sup> and decreased with depth. The only exception was soil from site no. 52, in which the mercury content in the surface horizon was 26 mg·kg<sup>-1</sup>, and in deeper horizons increased to over 600 mg·kg<sup>-1</sup>, which is probably linked with the earlier reclamation activities in the area. The observed trend of the decreasing mercury content with depth is similar to the results obtained by other authors [6, 7], where it was shown that mercury accumulates mainly in the surface part of soil and its content decreases with depth, with the exception of the case when the host rock yields increased amounts of this element. This relationship points to the strong binding and accumulation of mercury by humus compounds. This fact is also confirmed by statistic analysis, which indicates that there is a distinct positive correlation ( $r=0.84$ ) between the total mercury content and the organic carbon content. Statistic analysis of the correlation between the mercury content and the reaction of the analyzed soils did not show any significant relationship.

The obtained results of determination of total mercury concentration were compared with the allowable concentrations defined in the Minister of the Environment Directive [11].

According to this Regulation the soil is regarded as polluted by mercury if the mercury content in the upper layer of the soil exceeds 2 mg·kg<sup>-1</sup> on agricultural, urban land forest (group B) and 30 mg·kg<sup>-1</sup> on industrialized areas (group C).

Limit values for mercury established for soils of group B were exceeded in the majority of soil samples. However, limit values established for soils of group C were exceeded in the nine of twenty soil samples.

This Regulation regards total mercury concentration rather than individual mercury species. Determination of the total concentration of mercury in the soil is not sufficient and does not provide full information on the toxicity and bioavailability and gives information only on the state of pollution. However, the potential toxicity of mercury in the soil depends on its speciation and availability.

Twelve samples were selected for the sequential extraction; the total mercury content in these samples was within 2–252 mg·kg<sup>-1</sup>. Samples of soils, in which the mercury content was beyond the measurement range of the apparatus, i.e. exceeded 600 mg·kg<sup>-1</sup>, were not considered in further analysis, because lack of a precise mercury content would hamper the interpretation of results obtained in particular extraction stages.

Table 2. Mercury content and basic properties of the studied soils

Site no.	depth [cm]	Hg [mg·kg <sup>-1</sup> ]	pH in H <sub>2</sub> O	pH in KCl	C org [%]
15/17	0–20	34.2	5.2	4.2	2.77
	20–40	33.1	5.1	4.1	0.69
	40–60	11.7	4.9	4.0	0.70
	60–80	8.55	4.8	4.1	0.55
30	0–20	62.9	7.1	6.8	3.05
	20–40	2.00	7.2	7.1	0.42
	40–60	0.590	7.0	6.5	0.22
	60–80	0.710	6.9	6.7	0.46
52	0–20	26.1	5.6	4.6	3.43
	20–40	>600	5.0	4.1	2.80
	40–60	>600	6.6	6.2	1.68
	60–80	>600	6.6	6.0	1.78
55	0–20	77.8	6.6	5.9	1.22
	20–40	57.1	7.9	7.9	0.72
	40–60	1.33	7.3	7.2	0.43
	60–80	0.620	7.2	6.8	0.11
63	0–20	252	7.2	7.0	1.89
	20–40	13.7	7.8	7.7	0.65
	40–60	11.1	7.4	7.4	1.29
	60–80	7.90	7.0	6.6	0.62

A reference batch was also applied in sequential extraction; this material comprised soil NIST Soil Montana 2711 with a certified total mercury content ( $7.42 \pm 0.18 \text{ mg} \cdot \text{kg}^{-1}$ ). The recovery, i.e. the relation of the sum of particular mercury fractions to the total content measured directly using the AMA-254 analyzer was calculated for all samples. For six samples the results were satisfactory within the range of 84–110% (Table 3). For the remaining six samples the results were in the range of 34.8–77.9%, whereas for the certified reference material, the recovery was 81.4%.

Soil samples with low recovery values were characterized by high content of organic carbon and low pH, which indicate the presence of fulvic acids in the water solutions. These samples were collected from sample sites where peat and other compounds were not introduced to soil for remediation purposes. Additionally, the soils yielded metallic mercury, which was introduced to the soil by post-production fluids, a result of inappropriate management of sewage and wastes from technological processes. The presence of this form of mercury in the analyzed samples could be the reason of its evaporation during subsequent stages of sequential extraction.

For samples with satisfactory recovery values, sequential analysis of mercury was done; it indicated that for most analyzed soils and the certified reference batch the dominant was the mercury fraction linked with sulphides (31.7–88.1%) (chart 1). These results are in accordance with the data obtained by other authors [3], where the highest observed content had mercury linked with sulphides for samples collected from the same area and analyzed with application of other extraction techniques. However, the obtained values of mercury linked with sulphides are almost twice higher than those obtained previously, which may show that the applied solution of hydrochloric and nitric acids is not selective enough to determine the mercury content in this fraction and probably extracts also mercury from the residual fraction.

A relatively high content in the studied soils had also mercury linked with organic matter (3.45–26.0%); its distribution in the soil profile was almost proportional to the distribution of the total mercury content. Statistic analysis of the obtained results showed also that the content of mercury soluble in water displays a significant positive correlation with mercury linked with organic matter ( $r=0.77$ ) and organic carbon content (0.83). These relationships may indicate that most probably mercury of this fraction forms easily soluble complexes with organic compounds and to a lesser degree occurs in a form of soluble inorganic ion compounds. This fact is also confirmed by results obtained by other authors [2, 12, 13]. The content of mercury forms soluble in water was in the range of  $0.054\text{--}0.726 \text{ mg} \cdot \text{kg}^{-1}$ , whereas the percentage content of the more mobile forms of mercury (F1 and F2) did not exceed 1.5% of its total content. Determination of mercury in solutions obtained from two last stages of the extraction was hampered by the fast destruction of elements of the AMA-254 analyzer, resulting from the high concentration of the applied acids. Due to this fact it is not advisable to determine the two last fractions of mercury using this apparatus and it is indispensable to restrict the measurements to potentially available fractions or to change the detection method.

## CONCLUSIONS

The studies have shown distinct variability in mercury accumulation in the analyzed soils. Its total content varied from  $0.59 \text{ mg} \cdot \text{kg}^{-1}$  to over  $600 \text{ mg} \cdot \text{kg}^{-1}$ , with the highest values for

Table 3. Content of particular mercury fractions (n=3) in the total content [mg·kg<sup>-1</sup>]

Sample no.	No. of sampling site	Depth [cm]	F1	F2	F3	F4	F5	ΣF1-F5	Total content	Recovery [%]
1	15/17	0-20	0.101±0.012	0.118±0.008	1.57±0.13	9.74±0.44	1.11±0.06	12.6	36.3	34.8
2		20-40	0.287±0.014	0.078±0.004	0.628±0.064	15.8±0.7	1.15±0.05	17.9	30.6	58.6
3		40-60	0.060±0.007	0.011±0.004	0.417±0.063	9.97±0.37	0.852±0.066	11.3	11.7	96.6
4		60-80	0.080±0.009	0.036±0.003	0.437±0.059	7.05±0.38	0.529±0.055	8.13	8.55	95.1
5	30	0-20	0.104±0.009	0.123±0.008	5.85±0.49	16.4±0.6	25.9±1.4	48.4	62.9	76.9
6	52	0-20	0.474±0.030	0.246±0.028	6.36±0.38	9.61±0.69	7.75±0.50	24.4	26.1	93.5
7	55	0-20	0.527±0.039	0.184±0.014	8.50±0.37	5.30±0.14	42.7±1.9	57.2	77.8	73.6
8		20-40	0.726±0.037	0.708±0.086	7.95±0.65	5.41±0.28	29.7±1.4	44.5	57.1	77.9
9	63	0-20	2.02±0.11	0.357±0.054	18.7±0.5	90.6±3.1	7.69±0.21	119	252	47.3
10		20-40	0.112±0.011	0.059±0.007	1.71±0.08	9.12±0.52	1.04±0.07	12.0	13.7	87.9
11		40-60	0.147±0.018	0.028±0.003	0.826±0.035	9.34±0.39	0.683±0.022	11.0	11.1	99.3
12		60-80	0.111±0.008	0.087±0.012	0.298±0.116	7.25±0.28	0.905±0.068	8.65	7.90	109.5
SRM 2711			0.010±0.001	0.010±0.001	0.038±0.002	4.62±0.30	1.21±0.04	5.88	7.22	81.4

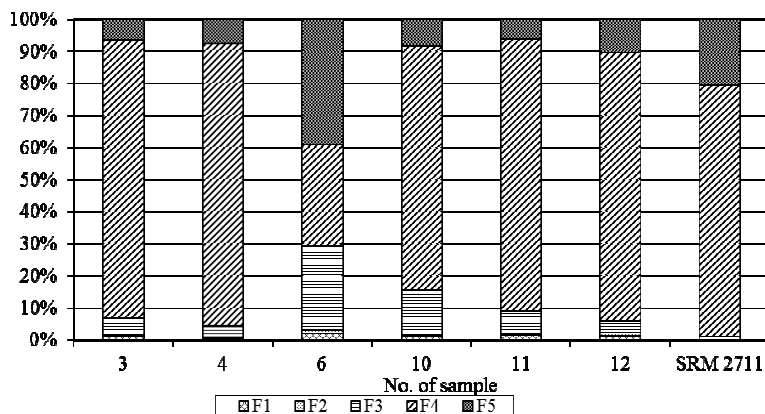


Fig. 2. Percentage content of different forms of mercury in soils in comparison with the total content

most samples observed in the surface soil horizons (0–20 cm). Modified Wallschläger sequential extraction of mercury applied in the analysis showed relatively high recovery values for most samples (84–110%), and the conducted sequential analysis of mercury indicated that most mercury was linked with the sulphide fraction. The average content of the mobile forms of mercury did not exceed 1.5% of its total content. During determination of mercury in solutions from the two last stages of extraction, fast destruction of the elements of analyzer AMA-254 was observed, which resulted from the application of strong acids. Due to this fact it is indispensable to restrict the measurement to fractions that are potentially available or to change the detection method.

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#### ZMODYFIKOWANA METODA EKSTRAKCJI SEKWENCYJNEJ WALLSCHLÄGERA, JAKO NARZĘDZIE DO OCENY MOBILNOŚCI RTĘCI

Celem podjętych badań była ocena przydatności wybranej metody ekstrakcji sekwencyjnej rtęci do oceny biodostępności rtęci w glebach zanieczyszczonych tym pierwiastkiem.

Do badań pobrano próbki glebowe z warstw 0–20 cm i 20–80 cm. Przeprowadzono analizę podstawowych właściwości fizycznych i chemicznych badanych gleb, oznaczono całkowitą zawartość rtęci oraz wykonano ekstrakcję sekwencyjną rtęci według zmodyfikowanej pięcioetapowej metody Wallschlägera.

Na podstawie dokonanych analiz stwierdzono, że badane gleby charakteryzowały się zróżnicowanymi zawartościami rtęci, przy czym największe jej zawartości stwierdzono w powierzchniowych warstwach gleby. Przeprowadzona ekstrakcja sekwencyjna rtęci w glebach wykazała, że największy procentowy udział w całkowitej zawartości rtęci stanowiła rtęć związana z siarczkami. Zaobserwowano także znaczący udział rtęci związanej z materią organiczną. Zawartość rtęci w formie biodostępnej nie przekraczała 1,5% zawartości ogólnej.