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Impact of the Municipal Solid Waste Łubna Landfill on Environmental Pollution by Heavy Metals

Barbara Gworek [1], Wojciech Dmuchowski [2,3], Eugeniusz Koda [4,*], Marta Marecka [1], Aneta H. Baczewska [3], Paulina Brągoszewska [1], Anna Sieczka [4] and Piotr Osiński [4]

1 Institute of Environmental Protection-National Research Institute, Krucza 5/11d St., Warsaw 00-548, Poland; barbara.gworek@ios.edu.pl (B.G.); marta.marecka@ios.edu.pl (M.M.); paulina.bragoszewska@ios.edu.pl (P.B.)
2 Department of Agriculture and Biology, Warsaw University of Life Sciences, Nowoursynowska 159 St., Warsaw 02-776, Poland; w.dmuchowski@obpan.pl
3 Polish Academy of Sciences, Botanical Garden—Center for Biological Diversity Conservation, Prawdziwka 2 St., Warsaw 02-973, Poland; a.baczewska@obpan.pl
4 Department of Geotechnical Engineering, Warsaw University of Life Sciences, Nowoursynowska 159 St., Warsaw 02-776, Poland; anna_sieczka@sggw.pl (A.S.); piotr_osinski@interia.pl (P.O.)
* Correspondence: eugeniusz_koda@sggw.pl; Tel.: +48-22-593-5218

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Abstract: Landfills have been identified as potential sources of heavy metal pollution of the environment. The municipal solid waste Łubna landfill is one of the largest landfills in Poland. Its impact on heavy metal pollution (Cd, Pb, Zn, Cu, and Cr) of groundwater, soil and plants has been thoroughly evaluated. Elevated levels of contamination have not been recorded in the vicinity of the landfill. The concentrations of heavy metals in soil from the vicinity of the landfill were similar to the geochemical background levels for the forest and farming soils of central Poland. The concentrations of heavy metals in European goldenrod (*Solidago virgaurea* L.) and grasses (*Poaceae*) did not exceed the baseline concentrations and did not indicate environmental pollution by heavy metals. The levels of the metal concentration in groundwater did not exceed the standards established for water intended for consumption.

Keywords: municipal solid waste landfill; metal pollution; soil; groundwater; plant

1. Introduction

The storage of municipal solid waste in landfills is one of the oldest and most common methods of their disposal in Poland. Up to 95% of total municipal solid waste (MSW) collected worldwide is disposed in landfills [1]. In Poland, a total of 10,330 thousand Mg of MSW were collected in landfills in 2014 [2].

Environmental pollution by heavy metals is one of the most dangerous elements of contamination and is particularly hazardous to human health. The municipal solid waste landfills are potential sources of groundwater, soil and plant pollution by heavy metals [3–7]. The contribution of heavy metals from MSW in Poland in 2011 was assessed by Tałałaj [8] as follows: Pb—108.5 g/Mg, Cu—90 g/Mg, Zn—560 g/Mg, Cr—101.5 g/Mg, and Cd—2.24 g/Mg. Heavy metals are a serious threat if they are transported from the landfill to the environment.

Leachate is produced during the exploitation of the landfill and also after its closure. According to the Council Directive No. 1999/31/EC [9] on the landfilling of solid waste, leachate has been defined as "any liquid percolating through the deposited waste and emitted from or contained within a landfill". MSW landfills have eliminated some impacts of old practices (i.e., uncontrolled waste deposition without any protecting measures); however, such impacts as gas and leachate formation are still a major

challenge for the waste management process. In addition to potential health hazards, these concerns include fires and explosions, vegetation damage, unpleasant odors, landfill settlement, groundwater pollution, air pollution and global warming [1].

One metric ton of landfill MSW would generate 0.2 m^3 of leachate [8]. However, the qualities and the quantities of landfill leachate are influenced by the moisture content, site hydrology, landfill age, climatic conditions, and degree of waste stabilization [10]. They are the main sources of pollution in areas directly adjacent to the landfill. Presently, numerous engineering measures have been undertaken to restrict the dispersal of pollutants from the landfills, such as liners, capping, leachate drainage systems, and vertical barriers [11–14].

This investigation aimed to answer the following questions:

- What is the impact of the long-term use of an uncontrolled landfill on environmental pollution by heavy metals in groundwater, soil, and plants?
- Do installed protection systems effectively reduce environmental pollution by heavy metals around landfills?

2. Materials and Methods

2.1. Geological Structure and Hydrogeological Conditions of the Study Area

The "Łubna" landfill is located within the Warsaw Plain in the marginal zone of the plateau with terraces of the Vistula River. Two geomorphological units have been distinguished within the landfill and its closest vicinity: a denuded and non-denuded postglacial plateau and fluvial valleys. The non-denuded plateau is covered by glacial tills of the Mazovian-Podlasian Stadial and incised by numerous small valleys. The denuded plateau is characterized by an almost complete lack of glacial tills of the Mazovian-Podlasian Stadial, and its surface is covered by muds, varved clays and ice-dammed sands of the Maximal Stadial of the Mid-Polish Glaciation [15,16].

The geological structure of the MSW Łubna landfill indicates that the subsoil is stratigraphically and genetically variable. On the older deposits, whose top is located at approximately 80 m below the surface level, represented by motley clays, muds and sands (Neogene, Pliocene), lies glacial till from the South Polish Glaciations (Quaternary, Pleistocene). A complex of sandy-gravel sediments from the Mazovian Interglacial is located above this till and is overlain by a series of sediments from the Mid-Polish Glaciation, beginning with a thin bed (approximately 3 m) of glacial tills. This complex is overlain by two horizons of glacial tills of the Maximal and Mazovian-Podlasian stadials. The lower horizon is represented by consolidated, dense glacial tills with variable thicknesses. The upper part of the complex comprises unconsolidated glacial tills (sandy loams, clayey sands) of the Mazovian-Podlasian Stadial, which are 3–4 m thick and covered by a discontinuous horizon of surface sands of glaciofluvial origin with a largely variable thickness, from 0.5 (in the western part) to 15 m (in the northern part of the landfill) [17]. A geological cross-section through the subsoil in the vicinity of the landfill is presented in Figure 1.

Two Quaternary aquifer horizons have been noted in the study area: soil and usable. Moreover, the ice-dammed sediments separating the two aquifers contain thin, saturated sand interbeds.

The first groundwater horizon is related to the cover of subsurface fluvioglacial sands. The depth to the water table is within 0.1 to 1.8 m. Replenishment of this horizon completely depends on the rainfall infiltration. This groundwater aquifer still contains contaminants accumulated between 1978 and 1998 (prior to the construction of a vertical barrier) from the leachate of the landfill [18].

After the construction of a vertical infiltration barrier, the transport of leachate from the landfill to the first aquifer horizon and melioration ditches was eliminated. The barrier, with depths from 5.7 to 17 m (depending on the subsoil conditions), is made of bentonite material. The existing drainage, a new network of melioration ditches, and the barrier around the landfill have caused changes in the directions and velocities of the groundwater flow compared to the primary hydro-isohypse layout in the area. The effects were confirmed by analyzing collected monitoring data from piezometers.

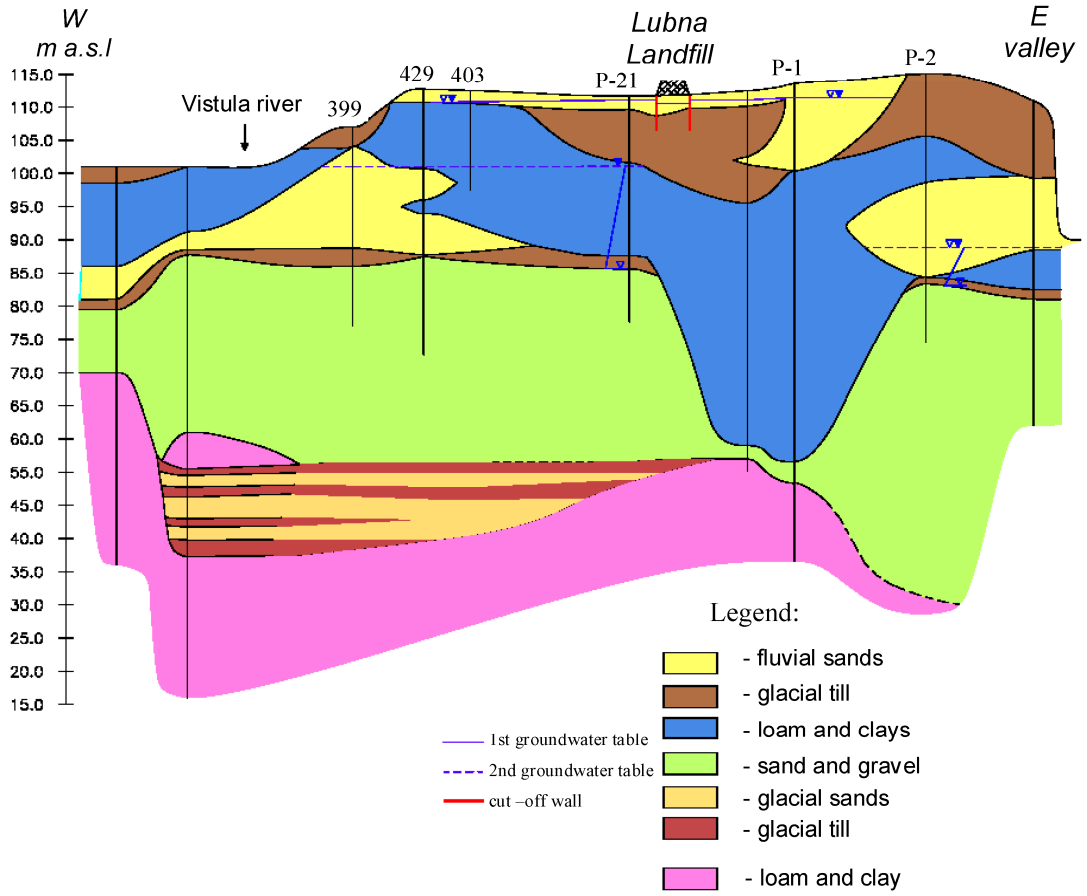

Figure 1. Geological cross-section through the subsoil of the MSW Łubna landfill and its vicinity [15].

Measurements in existing piezometers indicate that the directions of water flow are mainly to the north-west and south-east [15]. These directions are subject to seasonal oscillations that depend on the groundwater level of the first aquifer horizon [19]. Periodically, at high groundwater levels, water stagnates on the surface, forming local ponds. The filtration coefficients for soils in the first aquifer horizon are as follows: for fine and silty sands – $k = 3 \times 10^{-5}$ m/s, and for medium and coarse sands – $k = 2 \times 10^{-4}$ m/s [18].

2.2. History and Condition of the Landfill

The landfill is an embankment type structure, it covers the area of 16.2 ha, and its height exceeds 60 m above ground level. Storage of municipal waste in the MSW Łubna landfill began in 1978 in a wetland area that was not prepared for such purposes [20]. For the first 30 years, all municipal waste from the city was disposed on the landfill. However, after 1992, only commercial ballast and technological waste was stored there. Since 1996, protective and remediation works have been conducted within the landfill. The reclamation works were implemented according to the construction projects. They were simultaneously verified and updated according to observations of the physical and chemical processes within the landfill. The daily load of mixed solid municipal waste in the peak interval 1995–1998 reached 2500 Mg, whereas in the last years of the exploitation, it ranged from 400 to 700 Mg. As a result of protests by the neighboring community, the landfill was closed on 31 March 2011. Until 2014, works were conducted focusing on the formation and capping of the landfill surface and its biological remediation. In 2015, the final acceptance of the construction and remediation works occurred. Presently, attention is focused on the exploitation of the leachate drainage system, the degassing system, and maintenance of the vegetation on the landfill surface.

Since 1997, a systematic improvement of groundwater quality has been observed within the landfill area [16]. The improvement of groundwater and surface water quality around the landfill was obviously influenced by the construction of a drainage system for the leachates and a vertical bentonite barrier surrounding the landfill. The scheme of the remediation belt around the landfill is presented in Figure 2.

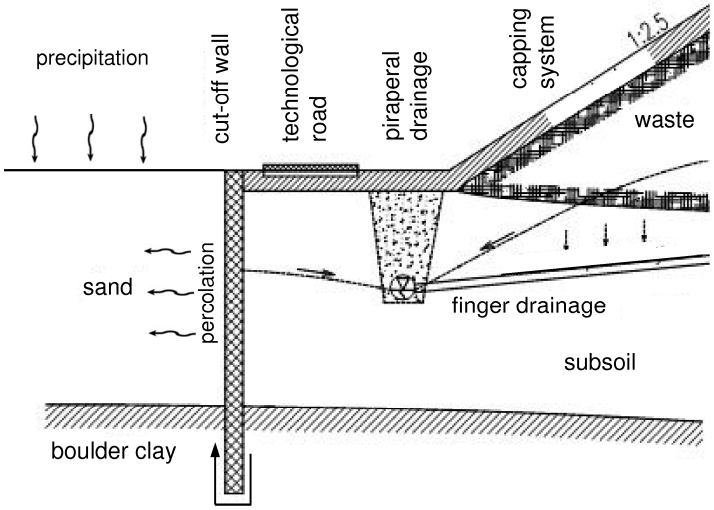

Figure 2. Scheme of the groundwater protection system against leachates from the MSW Łubna landfill [14].

The increase of groundwater quality is also influenced by the fact that the leachate has been transported to a municipal sewage plant since 1996. A local biological sewage plant was constructed for sewage treatment, but the expected treatment parameters were not achieved. In 2003, an exploitation permit was obtained to utilize the facility as a treatment sub-plant. Other options of leachate management were also considered (e.g., construction of a treatment plant with application of new technologies or a flow through a collector to the nearest municipal sewage treatment plant). Presently, the leachate is still removed by trucks to a municipal sewage treatment plant.

The study material included soils, plants and groundwater, in which the content of heavy metals was tested and included the following: Cd, Cu, Cr, Pb, and Zn. Six study plots with an area of 100 m^2 each were allotted for the analyses (Figure 3). Within each study plot, twelve squares with a 1 m side were selected, and soil and plant samples were collected from each plot for the chemical analyses. A piezometer for groundwater intake was also installed in each of the plots. For the groundwater quality assessment and determination of flow directions, samples were also collected from piezometers included in the groundwater monitoring network (Figure 3). The number of piezometers investigated was 12 [15].

The study plots were situated on all parts of the landfill: plot No. 1 was at a distance of 15 m, No. 2, 90 m; No. 3, 100 m; No. 4, 40 m; No. 5, 65 m; and No. 6, 250 m.

2.3. Methodology of the Study

Six samples of soil and plant leaves (grass from the family *Poaceae* sp. and European goldenrod, *Solidago virgaurea* L.) were collected in 2014 from each location. Both species predominated in the area of research. Soil samples were collected in 2014 from two depth intervals (0–0.25 m and 0.25–0.50 m).

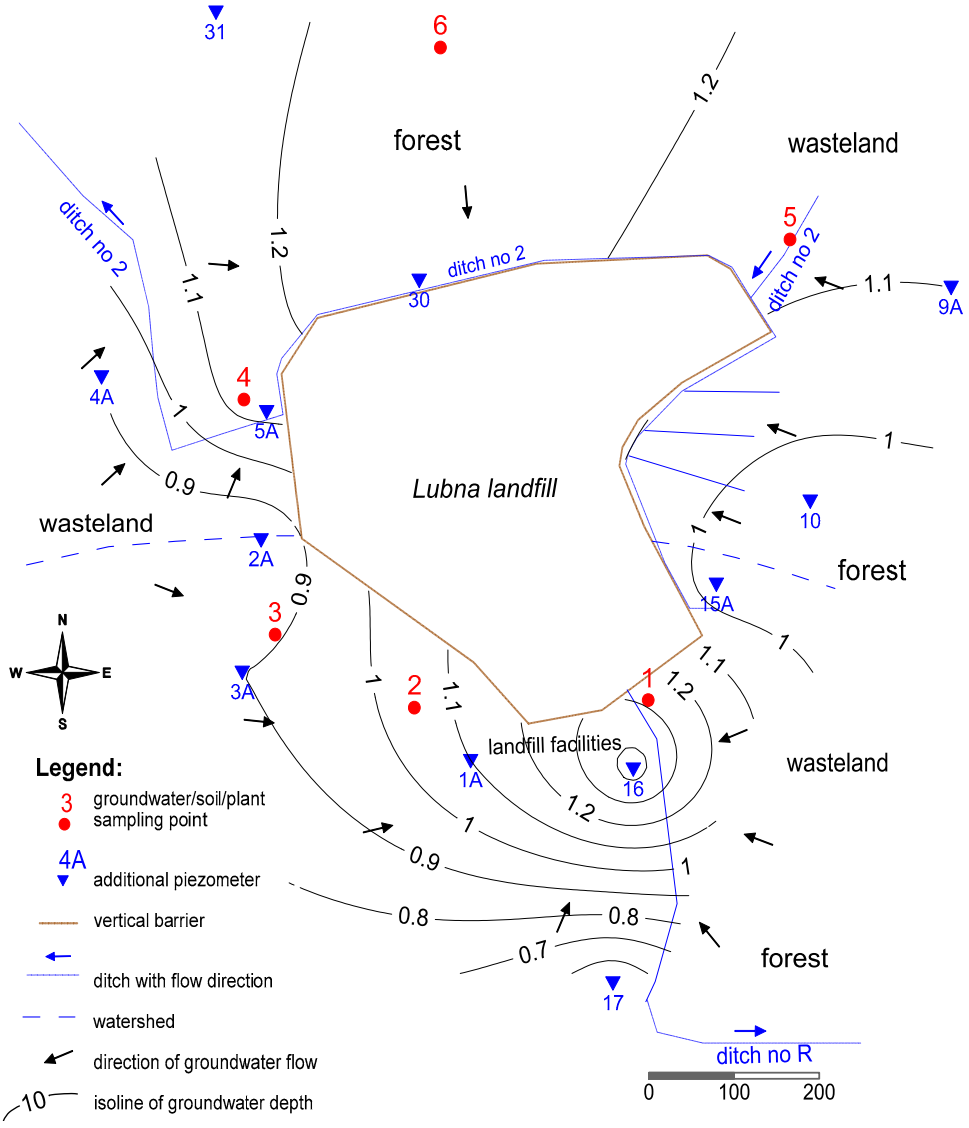

Figure 3. Location of the measurement points and additional piezometers with groundwater flow directions [15].

Subsequently, six plots of 1 m^2 were selected randomly within every research area. Six soil samples of 0.5 kg each from every analyzed depth were collected from all 1 m^2 plots, whereas plant samples were collected from the whole surface of the 1 m^2 plot, i.e., all the plants growing on the plot were cut and analyzed. Mixed samples for analysis were prepared from all the collected individual samples of soil and plant leaves. The soil was dried at 20–22 °C then sifted through a 1 mm sieve, so the material that was analyzed had a diameter of less than 1 mm. The plant samples were washed for one minute in distilled water before being dried (50 °C) and ground. Concentrated HNO3 (suprapur, Merck) (6 mL) and 2 mL of concentrated HCl (suprapur, Merck, Kenilworth, NK, USA) were added into 0.5 g of dried and ground soil and plant samples [21]. The samples were mineralized in a Speedwave Four microwave mineralizer by Berghof. The total time of mineralization was 66 min., and the maximum temperature was 220 °C. After mineralization, the samples were transferred to small flasks with a capacity of 50 mL and filled with MilliQ water to the fill line. Such solutions were analyzed using the ICP-OES technique (Vista-Pro Axial spectrometer by Varian). The obtained results were converted to dry weight and determined at 105 °C.

The groundwater samples were collected using an immersed pump from piezometers from the depth interval of 0.25–0.75 m below the surface [16,17]. The groundwater monitoring network consists

of three piezometers located on the east side of the landfill (9A, 10, 15A), then within the zone of groundwater discharge from the landfill there are seven piezometers, three on the south (1A, 16, 17) and four on the west side of the landfill (2A, 3A, 4A, 5A). The last two instruments are located on the north where the ground water inflow was defined, these being piezometers no 30 and 31. The full location of sampling points is presented in Figure 3. These 12 piezometers (triangle blue spots in Figure 3) were used to measure groundwater table and flow direction changes [15]. For the purpose of this presented study, six representative piezometers (circle red spots) were selected for further groundwater chemical analyses. Samples were collected in the years 1995, 1998, 2001, 2004, 2006, 2009, 2012, and 2014. Four samples of water were collected from each location. The measurement of heavy metals was commenced straight after the sample is collected. The water samples supplied to the laboratory were acidified with HNO_3; next the samples were subject to exposition in a UV mineralizer MINERAL for 1.5 h. After mineralization the samples were transferred to polyethylene bottles. Such samples were analyzed in a ICP-OES spectrometer (Vista-Pro Axial). To assure the appropriateness of sampling, each pumping was accompanied with simultaneous measurement of pH, temperature and electric conductivity. These samples were collected into smoked glass bottles, and stored at a temperature 1–5 °C. On the basis of the data obtained from the monitoring network, before and after the vertical barrier was constructed, it was possible to compare the water quality in respect of metal content in groundwater. The assessment of the groundwater quality within the landfill site was based on a comparison of metal concentration measured in collected samples (from six sampling points presented in Figure 3) with levels required in Polish Standards. The statistical *t*-test was performed to determine if means of values of groundwater quality from the periods 1994–1998 to 1999–2014 differ significantly. For the adopted significance level $p < 0.05$, it was stated if there was a measured difference between two groups (before and after the closure of the vertical barrier). The statistical significance was determined on the basis of the *t*-test results.

Chemical analyses were performed in a laboratory accredited for applying this procedure, according to the ISO 17O25. To provide quality control (QC), the elemental contents in the plant samples were determined using certified reference materials from NIST-USA Montana II Soil (SRM 2711a) and the Institute of Nuclear Chemistry and Technology—Poland, Tea Leaves (INCT-TL-1). The obtained results were in good agreement with the certified values. The recovery range was from 96% to 99% with an accuracy of 2% to 4%.

Biological indices are a good tool for the assessment of pollution by metals, their accumulation and interaction in the environment, as well as their mobility and translocation. The following indices were calculated:

- Biological Accumulation Coefficient (BAC), which expresses the ratio of metal concentration in plants to its concentration in soil (0–0.25 m):

$$BAC = Me_{plant}/Me_{soil(0\text{-}25\ cm)}$$

- Mobility Ratio, which expresses the ratio of metal concentration in soil (0–0.25 m) to its concentration in groundwater:

$$MR = Me_{soil(0\text{-}25\ cm)}/Me_{groundwater}$$

3. Results and Discussion

Landfills are sources of groundwater, soil and plant pollution due to the production of leachate and its migration through refuse [22–26].

The analyses of groundwater from piezometers located around the landfill (Table 1) indicated very low concentrations of heavy metals.

Table 1. Average values and standard deviations for concentrations of heavy metals, pH and EC in groundwater, 1994–2014.

Element	Polish Standard [27]	Average Concentration in Groundwater (mg/L) during Monitoring Period						
	(mg·dm^{-3})	1	2	3	4	5	6	All Piezometers
				1994–1998				
Cd	0.005	-	0.0008 ± 0.0009	0.007 ± 0.003	0.0005 ± 0.0003	0.0008 ± 0.0007	-	0.0023 ± 0.0012
Pb	0.025/0.010	-	0.011 ± 0.007	0.080 ± 0.075	0.015 ± 0.014	0.035 ± 0.059	-	0.035 ± 0.039
Cr	0.050	-	0.024 ± 0.042	0.531 ± 0.512	0.023 ± 0.007	0.047 ± 0.075	-	0.156 ± 0.159
Cu	2.0	-	0.110 ± 0.097	0.226 ± 0.169	0.104 ± 0.088	0.127 ± 0.130	-	0.141 ± 0.121
Zn	-	-	0.204 ± 0.089	0.586 ± 0.351	0.227 ± 0.183	0.615 ± 0.894	-	0.408 ± 0.379
pH	6.5–9.5	-	6.91 ± 0.29	7.36 ± 0.38	6.83 ± 1.21	7.45 ± 0.27	-	7.06 ± 0.42
EC	2500 (μS·cm^{-1})		1045 ± 403	14403 ± 5417	1110 ± 279	1638 ± 150	-	4549 ± 1562
				1999–2014				
Cd	0.005	0.0006 ± 0.0005	0.0004 ± 0.0003	0.0008 ± 0.0009	<0.0003 ± 0.0003	0.0005 ± 0.0003	0.0004 ± 0.0002	0.0005 ± 0.0004
Pb	0.025/0.010	0.005 ± 0.002	0.006 ± 0.003	0.019 ± 0.023	<0.004 ± 0.002	<0.004 ± 0.003	<0.004 ± 0.003	0.008 ± 0.011
Cr	0.050	<0.010 ± 0.045	<0.010 ± 0.045	0.216 ± 0.250	<0.010 ± 0.004	<0.010 ± 0.047	<0.010 ± 0.045	0.044 ± 0.073
Cu	2.0	0.015 ± 0.016	0.010 ± 0.016	0.037 ± 0.065	0.009 ± 0.011	0.017 ± 0.024	0.013 ± 0.036	0.017 ± 0.028
Zn	-	0.086 ± 0.054	0.059 ± 0.028	0.109 ± 0.094	0.190 ± 0.133	0.167 ± 0.130	0.068 ± 0.083	0.113 ± 0.087
pH	6.5–9.5	6.92 ± 0.32	6.07 ± 0.50	7.03 ± 0.34	7.37 ± 0.31	6.91 ± 0.46	6.62 ± 0.38	6.61 ± 0.38
EC	2500 (μS·cm^{-1})	7394 ± 3231	898 ± 506	6349 ± 3311	957 ± 189	1064 ± 519	198 ± 155	2810 ± 1319

The selected sampling points are those located in the vicinity of groundwater monitoring piezometers. There are also results for pH and electric conductivity (EC), provided to prove that the samples were not influenced only by the runoff or precipitation. The top soil layer consists mainly of a thin impermeable soil that limits the infiltration. However, there is still a possibility that pH and EC could be influenced by external pollution sources, such as industrial facilities in the close vicinity. In none of the analyzed groundwater samples did the metal concentration, in 2014, exceed the admissible values given in the Regulation of the Minister of Health, dated 13 November 2015, for the quality of water intended for human consumption [27]. Metals deposited in landfills are only released in small quantities and transferred to the leachates, and their release is restricted by processes favoring metal immobilization, such as sorption, precipitation and higher pH [8].

The *t*-test revealed that the differences between the measured parameters, before and after the vertical barrier was closed, are predominantly statistically significant (Table 2).

Table 2. *t*-test results for determination statistical significance of the difference between periods 1994–1998 and 1999–2014.

Parameter	*t*	Df	Standard Error of the Difference	Two-Tailed *p*-Value	95% Confidence Interval of the Difference	Statistical Significance of the Difference
Piezometer 2						
Cd	2.37	48	0.00	0.022	0.00–0.01	0.01–0.05
Pb	3.43	48	0.00	0.001	0.00–0.01	0.001–0.01
Cr	0.85	48	0.02	0.397	−0.02–0.05	>0.05
Cu	6.44	48	0.02	<0.001	0.07–0.13	<0.001
Zn	8.87	48	0.02	<0.001	0.11–0.18	<0.001
pH	4.84	48	0.17	<0.001	0.49–1.19	<0.001
EC	0.81	48	180	0.419	−215.91–509.91	>0.05
Piezometer 3						
Cd	11,0	46	0.00	<0.001	0.005–0.007	<0.001
Pb	4.46	48	0.01	<0.001	0.03–0.09	<0.001
Cr	2.77	48	0.11	0.008	0.09–0.54	0.001–0.01
Cu	5.64	48	0.03	<0.001	0.12–0.26	<0.001
Zn	7.76	48	0.06	<0.001	0.35–0.60	<0.001
pH	2.58	48	0.13	0.013	0.07–0.59	0.01–0.05
EC	5.84	48	1380	<0.001	5282.11–10825.89	<0.001
Piezometer 4						
Cd	4.35	47	0.00	<0.001	0.0001–0.0003	<0.001
Pb	4.98	48	0.00	<0.001	0.01–0.02	<0.001
Cr	6.68	44	0.00	<0.001	0.01–0.02	<0.001
Cu	6.92	48	0.01	<0.001	0.07–0.12	<0.001
Zn	0.60	43	0.06	0.549	−0.09–0.16	>0.05
pH	2.46	44	0.22	0.018	−0.98–0.098	0.01–0.05
EC	1.62	43	94.4	0.113	−37.64–343.46	>0.05
Piezometer 5						
Cd	2.82	46	0.00	0.007	0.0001–0.0005	0.001–0.01
Pb	3.52	41	0.01	0.001	0.01–0.05	0.001–0.01
Cr	1.65	44	0.02	0.104	−0.01–0.08	>0.05
Cu	5.20	48	0.02	<0.001	0.07–0.15	<0.001
Zn	3.17	48	0.14	0.003	0.16–0.73	0.001–0.01
pH	2.78	44	0.19	0.008	0.15–0.93	0.001–0.01
EC	2.44	43	235	0.019	99.16–1048.84	0.01–0.05

The *t*-test showed that the differences of the values of the chromium concentration in piezometers 2 and 5, the electrical conductivity in piezometers 2 and 4 and the zinc concentration in piezometer 4 are not statistically significant. For the rest of the measured parameters, the differences of the values between the periods of 1994–1998 and 1999–2014 are defined as statistically significant (very or extremely), which means that the results obtained are unlikely to be due to chance or sampling error.

The charts (Figures 4–8) show the changes in the concentrations of the investigated metals in the groundwater in the years 1995–2014. A significant decrease of concentration could be observed after the construction of the vertical barrier and leachate drainage system. However, due to leachate pumping and transport to a treatment plant, a slight decrease was also noticed just before the reclamation works were implemented. Progressing improvement of water quality was observed in all piezometers after only a few years since the groundwater protection system was installed in the year 1998. Before 1998, the Polish standard of water quality [27] was exceeded in some piezometers for Cd, Cr, Cu, and Pb. The results indicate that the construction of the vertical barrier and leachate drainage system effectively reduced the spread of metals from the landfill.

Studies conducted in four landfills in western Norway [28] also showed no effect on the environmental pollution by metals (Cd—0.002–0.004 mg/kg, Cr—0.006–0.045 mg/kg, Pb—0.002–0.006 mg/kg). The level of Cr in groundwater was a bit higher than the levels of Cd, Pb and Hg, but was still low, remaining under the limits for drinking water according to the EU Directive. Similar results were obtained from the MSW landfill in Delhi, India [29] and Lagos, Nigeria [30].

The concentrations of Pb, Cd, Cr, and Ni were found to be below the detection limit in the groundwater samples. Studies in other locations have indicated that MSW landfills can significantly affect the contamination of groundwater with heavy metals: Ahmadabad (Cd—0.003, Pb—0.042 [31]; and Calcutta [32] in India; Ibb City in Jemen [33]; Cartagena in Colombia [34]; Vejen landfill in Denmark [35]; Ano Liosia landfill in Greece [36]; and Zagreb in Croatia [37]. The contents of all analyzed heavy metals (Table 3) in the subsurface soil horizon (0–25 cm and at 25–50 cm) were low, as is commonly observed for farmlands and forest areas in Poland [38]. In none of the measurement points has the content exceeded the admissible boundary values of metal concentrations in soils, determined in the Ordinance of the Ministry of the Environment of 9 September 2002 [39]. The subsurface soil horizon contained higher contents of all heavy metals in all measurement points compared to the deeper horizon. Earlier soil analyses (2009) in the vicinity of the MSW Łubna landfill have indicated higher levels of metal concentrations in soils (Cd—0.8–1.3 mg/kg, Cu—1.1–14.9 mg/kg, Pb—3–44 mg/kg, and Zn—17–113 mg/kg) but admissible levels were likewise not exceeded [40].

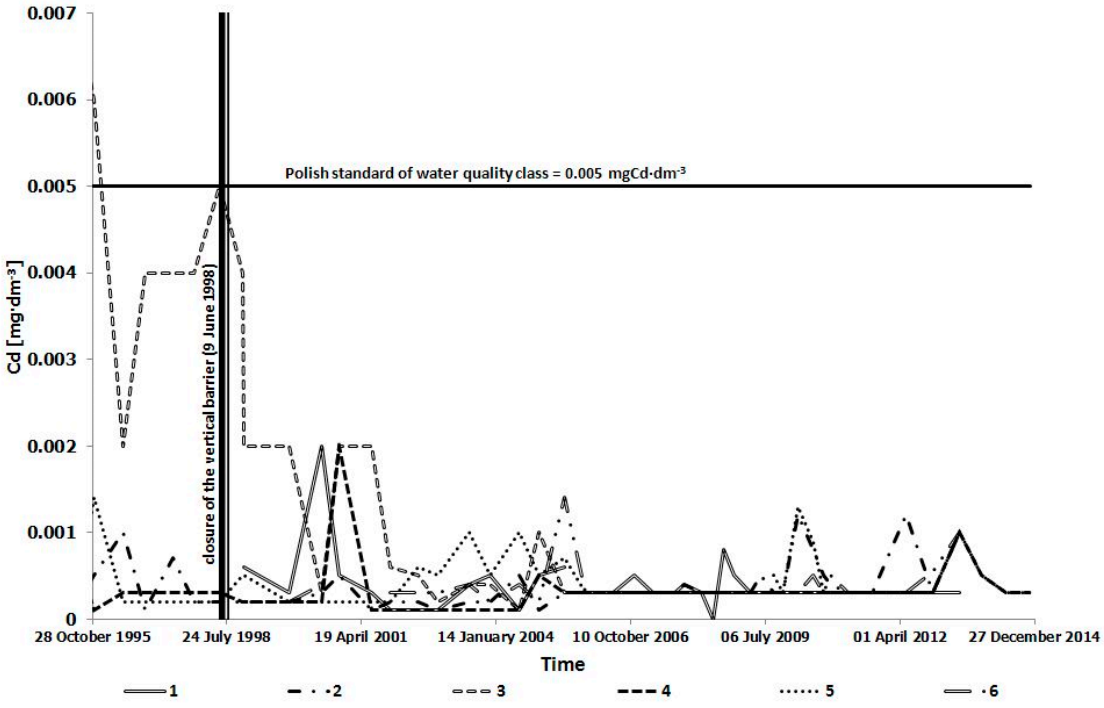

Figure 4. Changes of cadmium concentration in groundwater on MSW Łubna Landfill surroundings during monitoring period 1994–2014.

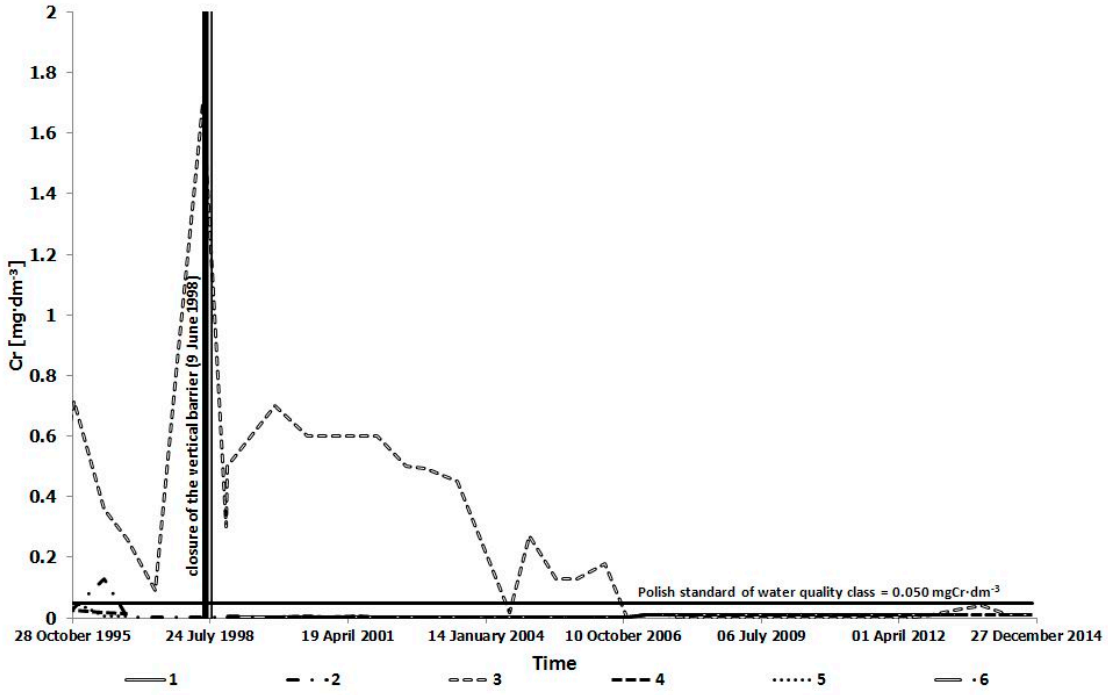

Figure 5. Changes of chromium concentration in groundwater on MSW Łubna Landfill surroundings during monitoring period 1994–2014.

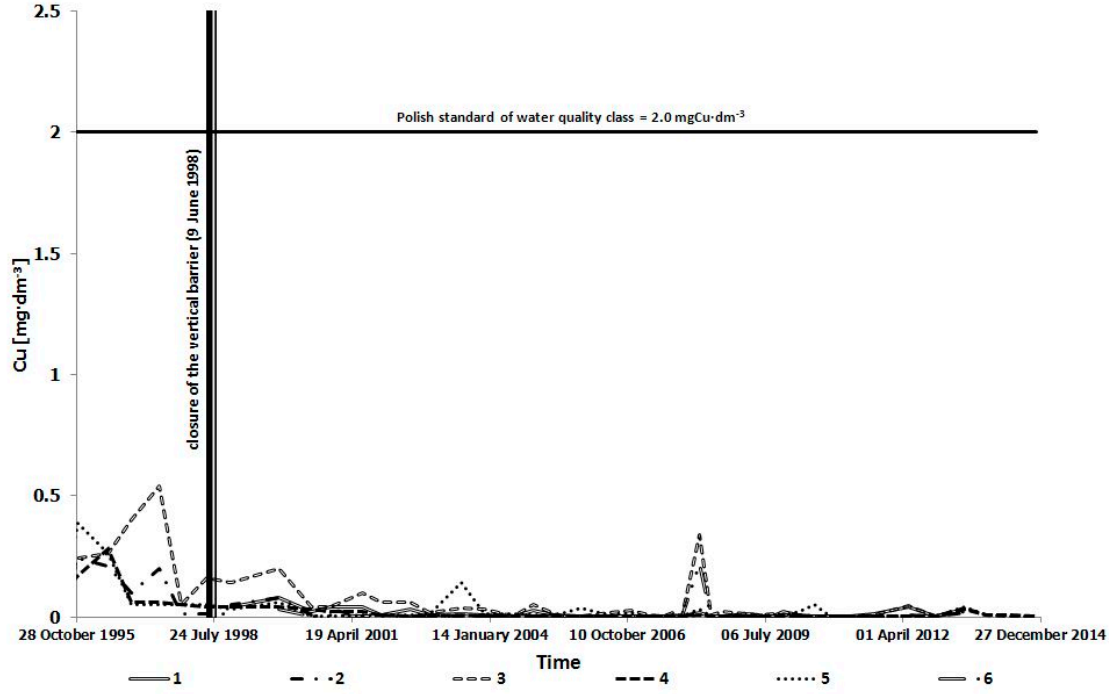

Figure 6. Changes of copper concentration in groundwater on MSW Łubna Landfill surroundings during monitoring period 1994–2014.

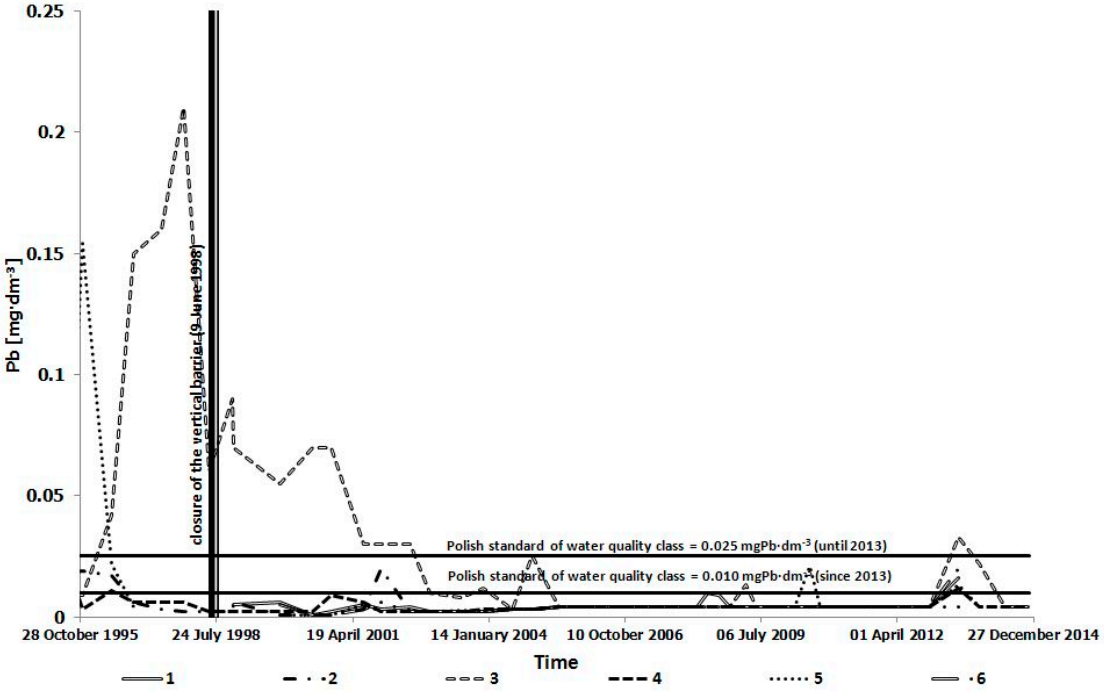

Figure 7. Changes of lead concentration in groundwater on MSW Łubna Landfill surroundings during monitoring period 1994–2014.

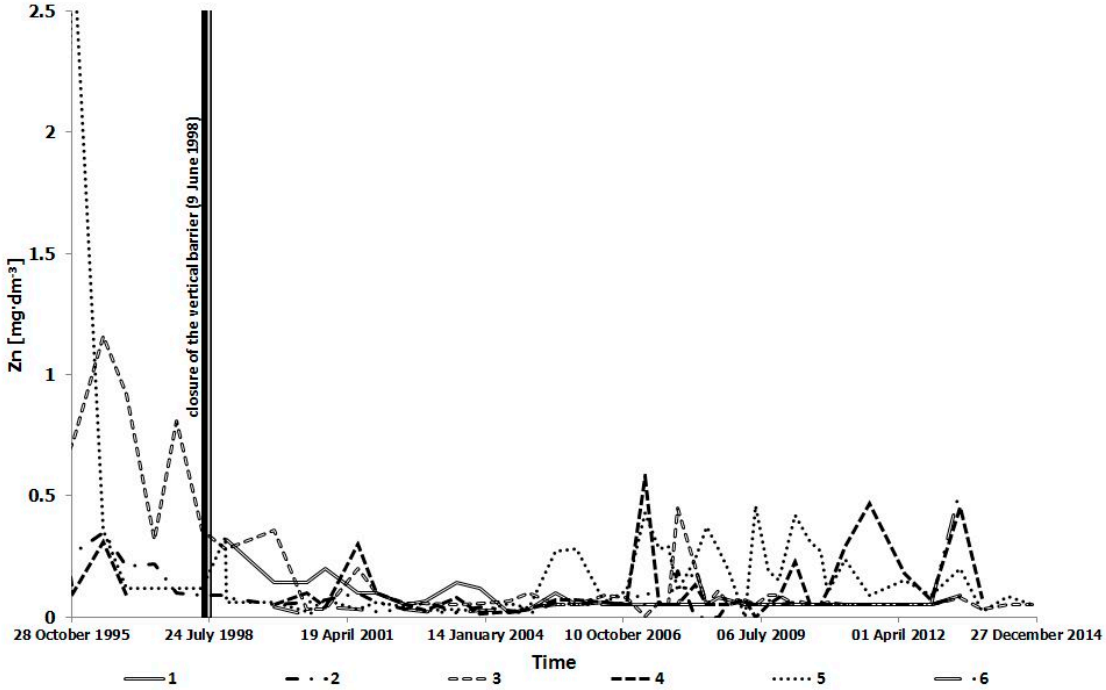

Figure 8. Changes of zinc concentration in groundwater on MSW Łubna Landfill surroundings during monitoring period 1994–2014.

Table 3. Average contents of heavy metals in the soil in the landfill area (mg/kg).

Plot No.	Depth (cm)	Cd	Cu	Cr	Ni	Pb	Zn
Background * Range Mean	**Surface Level**	**0.08–1.6 0.3**	**1–25 6**	**5–70 40**		**5–25 30**	**10–200 37**
1	0–25	0.274	2.67	4.5	2.1	21.0	11.0
	25–50	0.047	1.03	3.6	1.3	5.8	3.6
2	0–25	0.197	2.30	2.7	2.7	11.9	6.3
	25–50	0.098	1.21	3.3	1.6	3.2	2.3
3	0–25	0.334	5.70	9.9	9.2	31.7	32.3
	25–50	0.040	2.18	4.2	2.9	2.3	4.2
4	0–25	0.475	6.97	8.6	8.0	17.7	20.8
	25–50	0.286	4.23	8.5	7.9	7.4	18.0
5	0–25	0.080	2.97	1.7	1.2	4.4	5.2
	25–50	0.035	2.49	1.7	0.9	2.4	5.3
6	0–25	0.047	2.40	2.6	1.1	9.1	6.7
	25–50	0.038	0.86	2.1	1.1	4.5	5.2

Note: * Background level in sandy soils in Poland [38].

Table 4 presents the content of metals in the plants. The determined levels in the leaves and stems of European goldenrod and in grasses were low in all locations, as is appropriate for plants growing in Poland outside the direct influence of pollution emitters [38,41].

Table 4. Contents of heavy metals in European goldenrod (*Solidago virgaurea* L.) and grasses (Poaceae) in the area of the MSW Łubna landfill (mg/kg).

Plot No.	Plant	Cd	Cu	Cr	Ni	Pb	Zn
1	Grass	1.0	5.0	1.1	0.9	1.5	73
2	Grass	0.1	2.6	<0.2	<0.5	<0.6	31
	European goldenrod/leaves	0.4	3.7	<0.2	0.9	0.8	53
	European goldenrod/stem	0.4	2.6	<0.2	<0.5	<0.6	66
3	Grass	0.3	9.1	<0.2	<0.5	<0.6	78
	European goldenrod/leaves	0.2	5.9	<0.2	<0.5	<0.6	42
	European goldenrod/stem	0.3	5.9	<0.2	0.7	<0.6	36
4	Grass	0.3	10.9	<0.2	<0.5	4.6	30
	European goldenrod/leaves	0.4	10.7	0.2	1.6	2.3	84
	European goldenrod/stem	0.5	9.2	<0.2	0.7	1.9	92
5	Grass	0.4	6.2	<0.2	<0.5	2.6	60
	European goldenrod/leaves	0.3	9.7	0.3	0.6	2.4	90
	European goldenrod/stem	0.3	5.0	<0.2	<0.5	<0.6	85
6	Grass	0.1	7.3	<0.2	<0.5	<0.6	34
	European goldenrod/leaves	0.2	8.8	<0.2	0.7	0.9	55
	European goldenrod/stem	0.3	4.0	<0.2	0.5	<0.6	72

In the literature, there is little information on the accumulation of metals in European goldenrod. In uncontaminated agricultural areas, European goldenrod contained 30–68 mg/kg—Zn, 8.6–13.2 mg/kg—Cu [42], and in plants growing in the mountains of southern Poland, the leaves contained 49–88 mg/kg—Zn, 7.3–7.5 mg/kg—Cu, 1.9–2.1 mg/kg, 0.9–1.8 mg/kg—Cd, 3.0–4.2 mg/kg—Pb, 0.2–0.3 mg/kg—Cr [43].

Tables 5 and 6 present the values of biological indices. The Biological Accumulation Coefficient index reflects the ability of the plant to acquire metals from the soil [11]. Plants, for which the phytoaccumulation coefficient is (WF) > 1, are considered to be accumulators of a given element due

to their ability to intake and accumulate a metal in plant tissues. In the case of WF = 1 (approximately), the plants are considered as indicators of a given contaminant. Values below 1 characterize plants that restrict the intake of a given element. The analyses have shown that the intake of Cr, Ni and Pb by European goldenrod and grasses occurred in restricted quantities, and in these cases, the BAC values were below 1. In the cases of Cd, Cu and Zn, the values exceeded 1, but the contents of these metals in soil and plants indicate that, in the landfill area, the pollution is low and at a background level. The values of the Mobility Ratio, reflecting the infiltration of metals from soil to groundwater, were high, indicating an insignificant influence of the metal content in the soil on water pollution. In the scientific literature, no data assessing the value of the Mobility Ratio was found.

Table 5. Values of the phytoaccumulation coefficient—BAC (ratio of the metal concentration in plants to metal concentration in soil (0–25 cm)) in the area of the municipal solid waste Łubna landfill.

Plot No.	Plant	Cd	Cu	Cr	Ni	Pb	Zn
1	Grass	3.58	1.87	0.24	0.43	0.07	6.7
2	Grass	0.41	1.13	0.07	0.38	0.05	4.9
	European goldenrod/leaves	1.88	1.61	0.07	0.69	0.07	8.4
	European goldenrod/stem	2.13	1.13	0.07	0.38	0.05	10.5
3	Grass	0.31	1.60	0.02	0.05	0.02	2.4
	European goldenrod/leaves	0.29	1.04	0.02	0.05	0.02	1.3
	European goldenrod/stem	0.34	1.04	0.02	0.08	0.02	1.1
4	Grass	0.65	1.22	0.02	0.06	0.26	1.4
	European goldenrod/leaves	0.91	1.19	0.02	0.20	0.13	4.0
	European goldenrod/stem	0.97	1.32	0.02	0.09	0.11	4.4
5	Grass	4.75	2.09	0.12	0.42	0.59	27.1
	European goldenrod/leaves	3.75	3.27	0.18	0.50	0.55	17.3
	European goldenrod/stem	4.25	1.68	0.12	0.42	0.14	16.3
6	Grass	2.77	3.04	0.08	0.45	0.07	5.1
	European goldenrod/leaves	4.68	3.67	0.08	0.64	0.10	8.2
	European goldenrod/stem	5.96	1.67	0.08	0.45	0.07	10.8

Table 6. Values of the mobility ratio (ratio of metal concentration in soil (0–25 cm)) to its concentration in groundwater in the area of the MSW Łubna landfill.

Plot No.	Cd	Cu	Cr	Ni	Pb	Zn
1	456	178	447	39	4202	238
2	493	230	269	90	1983	126
3	418	154	114	1150	2113	310
4	1583	774	855	1337	4425	195
5	160	174	171	590	1105	31
6	116	184	262	1145	2276	108

The studies of Gworek et al. [16] have also not indicated environmental pollution by Hg caused by the MSW Łubna landfill. A lack of negative influence of the MSW Łubna landfill was most probably caused by the effectiveness of the installed protective measures against pollution dispersal (e.g., the bentonite vertical barrier) [14,15].

The recent records of the heavy metal concentrations within the containment system below the landfill are as follows: Cd = 0.049 (mg/dm^3); Pb = 0.66 (mg/dm^3); Cr = 1.44 (mg/dm^3); Cu = 0.18 (mg/dm^3); and Zn = 0.71 (mg/dm^3). These are the results from the sewage chemical analyses, which were pumped out from the containment below the landfill. All the values, except for Cu, exceeded the standards [27]. Based on these findings, it is clear that the engineering reclamation

solutions of the landfill sufficiently and effectively protect the areas around the landfill against the metals dispersal.

4. Conclusions

The studies of groundwater, soil and plant samples have indicated the lack of a significant influence of the MSW Łubna landfill on environmental pollution by heavy metals Cd, Cu, Cr, Pb, and Zn. The content of metals in the soil around the landfill was at a lower level than is common for farmlands and forest areas in Poland. In none of the measurement points did the content exceed the boundary admissible values of metal concentrations in soil. The levels of metals in the plants, i.e., the leaves and stems of European goldenrod (*Solidago virgaurea* L.) and grasses (*Poaceae*) were low and characteristic of plants growing beyond the direct influence of pollution emissions. The analysis of groundwater from piezometers located around the landfill has indicated very low concentrations of heavy metals. In none of the analyzed samples did the metal concentrations exceed the admissible values for the quality of water intended for human consumption. It is confirmed that the contaminants have been contained below the landfill body and are enclosed by the vertical barrier and natural impermeable soil layers.

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References

1. El-Fadel, M.; Findikakis, A.N.; Leckie, J.O. Environmental impacts of solid waste landfilling. *J. Environ. Manag.* **1997**, *50*, 1–25. [CrossRef]
2. Adamczyk, I.; Różańska, B.; Sobczyk, M. *Infrastruktura Komunalna w 2014 r. Environment*; Central Statistical Office: Warsaw, Poland, 2015.
3. Slack, R.J.; Gronow, J.R.; Voulvoulis, N. Household hazardous waste in municipal landfills: Contaminants in leachate. *Sci. Total Environ.* **2005**, *337*, 119–137. [CrossRef] [PubMed]
4. Baumann, T.; Fruhstorfer, P.; Klein, T.; Niessner, R. Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Res.* **2006**, *40*, 2776–2786. [CrossRef] [PubMed]
5. Prechthai, T.; Parkpian, P.; Visvanathan, C. Assessment of heavy metal contamination and its mobilization from municipal solid waste open dumping site. *J. Hazard. Mater.* **2008**, *156*, 86–94. [CrossRef] [PubMed]
6. Xie, S.; Ma, Y.; Strong, P.J.; Clarke, W.P. Fluctuation of dissolved heavy metal concentrations in the leachate from anaerobic digestion of municipal solid waste in commercial scale landfill bioreactors: The effect of pH and associated mechanisms. *J. Hazard. Mater.* **2015**, *299*, 577–583. [CrossRef] [PubMed]
7. Adhikari, K.; Pal, S. Assessment of Pollution Potential of Soil and Groundwater in a Non-Engineered MSW Landfill Site. *Intern. J. Environ. Sci. Dev.* **2016**, *7*, 207–210. [CrossRef]
8. Tałałaj, I.A. Release of Heavy Metals on Selected Municipal Landfill during the Calendar Year. *Ann. Set. Environ. Prot.* **2014**, *16*, 404–420.
9. Council Directive 99/31/EC of 26 April 1999 on the Landfill of Waste Entered. Available online: http://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:31999L0031 (accessed on 18 October 2016).
10. Kurniawan, T.A.; Lo, W.H. Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment. *Water Res.* **2009**, *43*, 4079–4091. [CrossRef] [PubMed]
11. Alagić, S.Č.; Šerbula, S.S.; Tošić, S.B.; Pavlović, A.N.; Petrović, J.V. Bioaccumulation of Arsenic and Cadmium in Birch and Lime from the Bor Region. *Arch. Environ. Contam. Toxicol.* **2013**, *65*, 671–682. [CrossRef] [PubMed]
12. Troschinetz, A.M.; Mihelcic, J.R. Sustainable recycling of municipal solid waste in developing countries. *Waste Manag.* **2009**, *29*, 915–923. [CrossRef] [PubMed]

13. Othman, E.; Yusoff, M.S.; Aziz, H.A.; Adlan, M.N.; Bashir, M.J.; Hung, Y.T. The effectiveness of silica sand in semi-aerobic stabilized landfill leachate treatment. *Water* **2009**, *2*, 904–915. [CrossRef]
14. Koda, E.; Osiński, P.; Kołanka, T. Flow numerical modeling for efficiency assessment of vertical barriers in landfills. In *Coupled Phenomena in Environmental Geotechnics*; Manassero, M., Dominijanni, A., Foti, S., Musso, G., Eds.; Taylor & Francis Group: London, UK, 2013; pp. 693–697.
15. Koda, E.; Osinski, P.; Sieczka, A.; Wychowaniak, D. Areal Distribution of Ammonium Contamination of Soil-Water Environment in the Vicinity of Old Municipal Landfill Site with Vertical Barrier. *Water* **2015**, *7*, 2656–2672. [CrossRef]
16. Gworek, B.; Dmuchowski, W.; Gozdowski, D.; Koda, E.; Osiecka, R.; Borzyszkowski, J. Influence of a Municipal Waste Landfill on the Spatial Distribution of Mercury in the Environment. *PLoS ONE* **2015**, *10*. [CrossRef] [PubMed]
17. Koda, E.; Pachuta, K.; Osiński, P. Potential of plants application in the initial stage of landfill reclamation process. *Pol. J. Environ. Stud.* **2013**, *22*, 1731–1739.
18. Koda, E. Influence of vertical barrier surrounding old sanitary landfill on eliminating transport of pollutants on the basis of numerical modelling and monitoring results. *Pol. J. Environ. Stud.* **2012**, *21*, 929–935.
19. Golimowski, J.; Koda, E. Assessment of remedial works effectiveness on water quality in the vicinity of Łubna landfill based on monitoring research. *Ann. Wars. Agric. Univ. Land Reclam.* **2001**, *32*, 17–30.
20. Allen, S.E.; Grimsha, W.H.N.; Parkinson, J.A.; Quarmby, C. *Chemical Analysis of Ecological Materials*; Blackwell Scientific Publications: Osney Mead, UK, 1974.
21. Ahmed, A.M.; Sulaiman, W.N. Evaluation of groundwater and soil pollution in a landfill area using electrical resistivity imaging survey. *Environ. Manag.* **2001**, *28*, 655–663.
22. Jain, P.; Kim, H.; Townsend, T.G. Heavy metal content in soil reclaimed from a municipal solid waste landfill. *Waste Manag.* **2005**, *25*, 25–35. [CrossRef] [PubMed]
23. Amusan, A.A.; Ige, D.V.; Olawale, R. Characteristics of Soils and Crops' Uptake of Metals in Municipal Waste Dump Sites in Nigeria. *J. Hum. Ecol.* **2005**, *17*, 167–171.
24. Kasassi, A.; Rakimbei, P.; Karagiannidis, A.; Zabaniotou, A.; Tsiouvaras, K.; Nastis, A.; Tzafeiropoulou, K. Soil contamination by heavy metals: Measurements from a closed unlined landfill. *Bioresour. Technol.* **2008**, *99*, 8578–8584. [CrossRef] [PubMed]
25. Mari, M.; Nadal, M.; Schuhmacher, M.; Domingo, J.L. Exposure to heavy metals and PCDD/Fs by the population living in the vicinity of a hazardous waste landfill in Catalonia, Spain: Health risk assessment. *Environ. Intern.* **2009**, *35*, 1034–1039. [CrossRef] [PubMed]
26. Aucott, M. *The Fate of Heavy Metals in Landfills: A Review*; New Jersey Department of Environmental Protection: Trenton, NJ, USA, 2006.
27. Regulation of the Minister of Health Dated 13 November 2015, on the Quality of Water Intended for Human Consumption. Journal of Laws 2015, item 1989. Available online: http://isap.sejm.gov.pl/DetailsServlet?id=WDU20150001989 (accessed on 18 October 2016).
28. Øygard, J.K.; Måge, A.; Gjengedal, E. Estimation of the mass-balance of selected metals in four sanitary landfills in Western Norway, with emphasis on the heavy metal content of the deposited waste and the leachate. *Water Res.* **2004**, *38*, 2851–2858. [CrossRef] [PubMed]
29. Mor, S.; Ravindra, K.; Dahiya, R.P.; Chandra, A. Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environ. Monit. Assess.* **2006**, *118*, 435–456. [CrossRef] [PubMed]
30. Longe, E.O.; Balogun, M.R. Groundwater quality assessment near a municipal landfill, Lagos, Nigeria. *Int. J. Environ Sci. Dev.* **2010**, *2*, 39–44.
31. Singh, U.K.; Kumar, M.; Chauhan, R.; Jha, P.K.; Ramanathan, A.L.; Subramanian, V. Assessment of the impact of landfill on groundwater quality: A case study of the Pirana site in western India. *Environ. Monit. Assess.* **2008**, *141*, 309–321. [CrossRef] [PubMed]
32. Biswas, A.K.; Kumar, S.; Babu, S.S.; Bhattacharyya, J.K.; Chakrabarti, T. Studies on environmental quality in and around municipal solid waste dumpsite. *Resour. Conserv. Recycl.* **2010**, *55*, 129–134. [CrossRef]
33. Al Sabahi, E.; Rahim, S.A.; Wan Zuhairi, W.Y.; Nozaily, F.A.; Alshaebi, F. The characteristics of leachate and groundwater pollution at municipal solid waste landfill of Ibb City, Yemen. *Am. J. Environ. Sci.* **2009**, *5*, 256–266. [CrossRef]

34. Olivero-Verbel, J.; Padilla-Bottet, C.; De la Rosa, O. Relationships between physicochemical parameters and the toxicity of leachates from a municipal solid waste landfill. *Ecotoxicol. Environ. Saf.* **2008**, *70*, 294–299. [CrossRef] [PubMed]
35. Christensen, T.H.; Kjeldsen, P.; Albrechtsen, H.-J.; Heron, G.; Nielson, P.H.; Bjerg, P.L.; Holm, P.E. Attenuation of landfill leachate pollutants in aquifers. *Crit. Rev. Environ. Sci. Technol.* **1994**, *24*, 119–202. [CrossRef]
36. Fatta, D.; Papadopoulos, A.; Loizidou, M. A study on the landfill leachate and its impact on the groundwater quality of the greater area. *Environ. Geochem. Health* **1999**, *21*, 175–190. [CrossRef]
37. Mikac, N.; Cosovic, B.; Ahel, M.; Andreis, S.; Toncic, Z. Assessment of groundwater contamination in the vicinity of a municipal solid waste landfill (Zagreb, Croatia). *Water Sci. Technol.* **1998**, *37*, 37–44. [CrossRef]
38. Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soils and Plants*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2001.
39. Regulation of the Ministry of Environment of 09 September 2002 Concerning Soil Quality Standards and Quality Standards of Soil. Journal of Laws 2002, No 165, item 1359. Available online: http://isap.sejm.gov.pl/DetailsServlet?id=WDU20021651359 (accessed on 18 October 2016).
40. Kondras, M.; Czepinska-Kaminska, D.; Chodkowska, A.; Chrzanowska, A. The ecotoxicological assessment of the soil in the area of Lubna waste landfill. *Rocz. Gleb.* **2010**, *61*, 105–112. (In Polish)
41. Dmuchowski, W.; Gazdowski, D.; Brągoszewska, P.; Baczewska, A.H.; Suwara, I. Phytoremediation of zinc contaminated soils using silver birch (*Betula pendula* Roth). *Ecol. Eng.* **2014**, *71*, 32–35. [CrossRef]
42. Kołodziej, B. Goldenrod (*Solidago virgaurea* L. ssp. *virgaurea*) reaction to foliar fertilization. *Ann. UMCS Agric.* **2008**, *63*, 1–9.
43. Łaszewska, A.; Kowol, J.; Wiechuła, D.A.; Kwapuliński, J. Bioaccumulation of metals in selected species of medicinal plants in the Silesian and Żywiec Beskids. *Problemy Ekologii* **2007**, *11*, 285–291. (In Polish)