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LONG-TERM CHANGES IN SURFACE AND GROUNDWATER QUALITY IN THE AREA OF A MUNICIPAL LANDFILL (BARYCZ, POLAND)

Data from 15-year lasting monitoring period was investigated to assess the impact of a municipal landfill on the aquatic environment (Barycz, Poland). Surface and groundwater samples were analyzed to determine basic parameters (pH, conductivity, BOD₅, COD, TOC, concentrations of NH⁴₄-N, ni-trates, phosphorous, and chlorides), and concentrations of metals (Cd, Cu, Cr, Hg, Pb, and Zn). Parameters characterizing the landfill impact on aquatic environment demonstrated elevated values at the surface waters, especially at sampling site localized directly downstream from the facility. However, detailed assessment of the extent of this impact has been hindered due to overlapping anthropogenic and natural factors. The direct impact of the landfill on groundwater was evident, but limited within the direct proximity of the facility. Due to the specific location of the landfill, at a former salt mining area, the hydrogeologic settings induced a more pronounced impact on surface and groundwater quality. The brine extrusions from the salt formations, due to the growing weight of the waste collected in the landfill, caused an increase in water salinity. The long-term monitoring effort illustrates that chloride contamination has been declining since discontinuation of the salt excavation, however, this depends greatly on the actual hydrogeological conditions in the salt mine.

1. INTRODUCTION

Major potential environmental threats posed by municipal landfills are pollution of ground water and surface water, mainly due to the contact of these environments with landfill leachate [1-3]. Since this leachate contains pollutants from various groups in high concentrations, i.e., dissolved organic matter, inorganic macrocomponents, and heavy metals [4-8], resultant impacts can be extensive and very harmful to the aquatic habitat. These implications for the environment should be normally mitigated through

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the engineered liners, leachate collection systems, and proper landfill management. However, in the case of unfavorable geological settings, the scale and extent of such an impact can be additionally amplified.



Fig. 1. Localization of the surface (M1–M4) and groundwater (area A–C) sampling sites in the Barycz landfill area (ca. 1:40 000). Arrows represent presumed directions of the groundwater flow (size of the arrow depicts probability of the influence)

The Barycz municipal landfill (southern Poland) was opened for use in 1974 at a former salt mining area, belonging to the Wieliczka Salt Mine. Establishment of this facility was a part of a post-mining reclamation plan, which today covers 36.5 ha, and is divided into three stages (Fig. 1). Stage I of the original dumping site had no environmental safeguards, i.e., the landfill base had no drainage system and was not sealed by any natural or artificial liners. This stage was later reclaimed by the end of 1992 by covering with layers of clay and soil, and sown with grass. Degassing chambers for this part of the landfill were built between 1992 and 1997. Stage II, opened in the late 1980s, which has been surrounded by a system of drainage ditches, and the landfill bowl was equipped with a surface drainage system. Leachate was collected into a leak-tight reservoir and regularly transferred to a waste water treatment plant. Parallel to the reclamation of stage II (2005), the expansion of the landfill site into stage III was designed in compliance with all the UE standards and has a life expectancy until 2018. Stage III has been equipped with an artificial two-layer insulation and a leachate collecting system to prevent any adverse impacts on surface and groundwaters.

At the former mining site, where the landfill has been established, salt was excavated from boulder (blocky) and stratiform (bedded) Barycz deposits. The blocky deposit has a form of a mass unstructured gangue with entrained boulders of rock salt, while the bedded one has a layered structure composed of different types of rock salt inter-bedded by claystone. These salt deposits are separated from the aquifers by a later formed buffer zone composed of silty claystones and gypsum. The whole rock-bearing complex was subjected to intense folding and tectonic deformations, as well as mining activities, leading to the formation of local channels enabling hydraulic contact between the brine and permeable water-logged deposits. Moreover, since the landfill facility was built on natural hollows and depressions, resulting from surface subsidence due to the salt leaching through boreholes, the growing overload from dumped waste escalated the chamber collapsing process and extrusion of brine through a system of cracks and fissures [9].

From a hydrological point of view, the mining/landfill area is located in the basin of the Vistula River with a main watercourse flowing through the landfill (Malinówka creek). This creek, in the upstream section, is fed by two watercourses and surface runoff from the catchment, where a household sewage collection system is based on individual septic tanks, and where accidental spills are possible. In this catchment, agricultural and animal husbandry activities are also performed. Moreover, this creek also drains groundwater in the valley bottom and its slopes. Downstream from the landfill, the Malinówka creek feeds other watercourses. During the launch of stage II, the Malinówka creek was moved away from the dumping area to reduce the landfill's impact on surface water.

The papers main goal was to verify long-term impact of the municipal landfill on the aquatic environment based on a 15-year lasting monitoring period. The study also aims to establish the relative importance and prevalence of its specific localization settings and hydrogeological conditions for the surface and groundwater quality in the Barycz landfill facility.

2. MATERIALS AND METHODS

Sampling system. The current study is based on the monitoring data on surface and ground water system during a 15-year period (1997–2011), being in possession of the Wieliczka Salt Mine. Its scope and extent had been modified accordingly to changes in the environmental control regulations, and currently fully reflect the UE regulations governing landfill monitoring issues.

The surface water monitoring sampling consists of 4 sampling sites localized on the Malinówka creek, upstream, midstream, and downstream (2 sites) from the landfill (Fig. 1, sites M1–M4). This system focuses on the status of the stream and it is supposed to enable a comparison between present levels of contamination downstream from the landfill from the background quality upstream of the facility. Samples have been collected 4 times per year (March, June, September, and November) by the Voivodship Inspectorate for Environmental Protection at Cracow, Poland (WIOŚ). The selection of

the indicators complies with the standard monitoring scheme adopted for such facilities, and consists of concentrations mainly of nitrogen compounds (ammonium nitrogen, and nitrate), and heavy metals (Cd, Cu, Cr, Hg, Pb, and Zn). Due to the specific localization of the landfill on the former salt mine, site chloride concentration was also included in the list of monitored parameters. Moreover, leachate samples collected directly from the draining installation were investigated within this monitoring system.

Currently, the groundwater monitoring system in the landfill area consists of 11 piezometers, sampled also four times per year by the WIOŚ. Piezometers C, P-2, P-3, P-6, and P-8, localized in the neighborhood of the landfill (Fig. 1, area A) hold the longest data record (1997–2011), while piezometers P-III-1, P-III-3, P-III-5, P-III-6, P-III-9 (Fig. 1, area B) were added to the monitoring network in 2005, after the opening of stage III. For the piezometers localized at the greatest distance from the landfill (G, S, Ł, 22, H, K, and S-6; Fig. 1, area C) the sampling effort was suspended in 2002. Survey effort within the entire monitoring system is focused on priority groundwater contaminants typical of landfill impact. This includes: major ion balance and minor chemical composition (inorganic and organic contaminants, including heavy metals).

Sample analyses. All parameters (pH, conductivity, BOD₅, COD, TOC, concentrations of NH₄⁺-N, nitrates, phosphorous, chlorides) except for heavy metals, were measured and determined according to the standards and methodology adopted in the accredited laboratories of the Inspectorate for Environmental Protection [10]. During analyses, calibration solutions, blanks, and standards were run every 10 samples. Precision was monitored by running duplicates of any two real samples placed in random order within every 10 samples. Replicate measurements agreed within less than 5%. To assess contamination, method and filtration blanks were randomly processed throughout the procedure. Mean values for blanks were below reported detection limits. Accuracy was assured through the use of an in-house reference material according to the PN-EN ISO 11885:2009 norm.

Heavy metal (Cd, Cu, Cr, Hg, Pb, and Zn) analyses were conducted in the certified Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology at the University of Science and Technology (AGH) at Cracow which follows quality assurance and analytical quality control program (PN-EN ISO/IEC 17025). Total metal concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) method in samples filtered using Sartorius 0.45 μ m filters and acidified by ultrapure HCl. Percentage recovery of metals, with respect to referred values, was in the 90–110% range.

General statistical analyses were produced using Excel v. 2013. To assess the relationship and significant differences among the individual series, an analysis of variance was performed using the Statgraphics Centurion XVII. Since, measured parameters generally displayed non-normal distribution, descriptive statistics were presented as median value and minimum-maximum range. Significant differences among series were assessed based on the Kruskall-Wallis test.

3. RESULTS

pHs of collected surface water samples were in the neutral-slightly alkaline range, with the maximum values not exceeding 8.5 (Table 1), which is typical of riverine waters in this part of the Vistula catchment [11]. For leachates and samples collected from the piezometers, the pH range was slightly broader (5.8–9.4, Table 1).

Table 1

Parameter	Surface water				
	M1	M2	M3	M4	
pH	7.9 (7.2–8.5)	7.7 (6.8–8.4)	8.1 (7.5-8.4)	7.8(7.4-8.3)	
BOD ₅ , mg·dm ⁻³	3.4 (1.0-246.5)	3.6 (0.7-230.8)	4.6 (1.1-203.2)	4.4 (1.2-70.1)	
COD, mg·dm ⁻³	24.3 (2.9-629.5)	25.3 (2.9–597.9)	33.0 (4.1–568.4)	30.9 (8.3-260.0)	
NO ₃ , mg ⋅ dm ⁻³	1.0 (0.1–19.5)	0.7 (0.2-6.0)	0.9 (0.2-6.9)	0.8 (0.2-4.9)	
NO_2^- , mg·dm ⁻³	0.1 (bdl-1.7)	0.1 (bdl-0.3)	0.1 (bdl-1.5)	0.1 (bdl-2.9)	
NH₄-N, mg·dm ⁻³	0.8 (0.1-8.8)	1.9 (0.1–29.4)	1.4 (0.1–207.2)	0.4 (0.1–96.1)	
Total P, mg·dm ⁻³	0.3 (0.1-3.3)	0.1 (1.7-32.2)	0.2 (0.1-1.6)	0.1 (bdl-0.5)	
TOC, mg·dm ⁻³	9.4 (5.1-272.0)	10.3 (1.5-249.1)	11.1 (5.1-240.7)	10.6 (4.4-57.0)	
Cl⁻, mg·dm⁻³	222 (56-39400)	450 (82-29840)	781 (185-30400)	855 (115-28200)	
Conductivity, µS·cm ⁻¹	1034 (60–94000)	1652 (420–96500)	1670 (6–95600)	2600 (14-78800)	
	Groundwater				
D (Groundwater		т 1 (
Parameter	Area A	Groundwater Area B	Area C	Leachate	
Parameter pH	Area A 6.80 (5.8–9.4)	Groundwater Area B 7.1 (6.4–8.0)	Area C 7.2 (6.0–8.9)	Leachate 8.2 (7.1–9.1)	
Parameter pH BOD5, mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8)	Leachate 8.2 (7.1–9.1) 698 (110–3480)	
Parameter pH BOD5, mg·dm ⁻³ COD, mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0)	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219)	
Parameter pH BOD ₅ , mg·dm ⁻³ COD, mg·dm ⁻³ NO ₃ , mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3_	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1)	
Parameter pH BOD ₅ , mg·dm ⁻³ COD, mg·dm ⁻³ NO ₃ , mg·dm ⁻³ NO ₂ , mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3 0.1 (bdl–0.4)	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9)	
Parameter pH BOD5, mg·dm ⁻³ COD, mg·dm ⁻³ NO3, mg·dm ⁻³ NO2, mg·dm ⁻³ NH4-N, mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2) 10.6 (0.1–286.7)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3) 0.8 (0.1–7.0)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3 0.1 (bdl–0.4) 1.1 (0.1–119.3)	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9) 934 (233–2025)	
Parameter pH BOD5, mg·dm ⁻³ COD, mg·dm ⁻³ NO3, mg·dm ⁻³ NO2, mg·dm ⁻³ NH4-N, mg·dm ⁻³ tot P, mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2) 10.6 (0.1–286.7) 0.1 (bdl–4.9)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3) 0.8 (0.1–7.0) 0.1 (bdl–1.2)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3_ 0.1 (bdl–0.4) 1.1 (0.1–119.3)	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9) 934 (233–2025) 0.1 (bdl–3.3)	
Parameter pH BOD5, mg·dm ⁻³ COD, mg·dm ⁻³ NO3, mg·dm ⁻³ NO2, mg·dm ⁻³ NH4-N, mg·dm ⁻³ tot P, mg·dm ⁻³ TOC, mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2) 10.6 (0.1–286.7) 0.1 (bdl–4.9) 7.4 (1.2–65.0)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3) 0.8 (0.1–7.0) 0.1 (bdl–1.2) 5.1 (1.7–34.4)	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3 0.1 (bdl-0.4) 1.1 (0.1–119.3) –	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9) 934 (233–2025) 0.1 (bdl–3.3) 876 (51–2933)	
Parameter pH BOD5, mg·dm ⁻³ COD, mg·dm ⁻³ NO ₂ , mg·dm ⁻³ NO ₂ , mg·dm ⁻³ NH ⁴ -N, mg·dm ⁻³ tot P, mg·dm ⁻³ TOC, mg·dm ⁻³ Cl ⁻ , mg·dm ⁻³	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2) 10.6 (0.1–286.7) 0.1 (bdl–4.9) 7.4 (1.2–65.0) 20 250 (7–218500)	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3) 0.8 (0.1–7.0) 0.1 (bdl–1.2) 5.1 (1.7–34.4) –	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3 0.1 (bdl–0.4) 1.1 (0.1–119.3) – – 38 (3–870)	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9) 934 (233–2025) 0.1 (bdl–3.3) 876 (51–2933) 3080 (560–5670)	
Parameter pH BOD ₅ , mg·dm ⁻³ COD, mg·dm ⁻³ NO ₃ , mg·dm ⁻³ NO ₂ , mg·dm ⁻³ NH ⁴ -N, mg·dm ⁻³ tot P, mg·dm ⁻³ TOC, mg·dm ⁻³ Cl ⁻ , mg·dm ⁻³ Conductivity,	Area A 6.80 (5.8–9.4) 3.9 (0.1–65.0) 71.3 (3.5–915.3) 0.3 (bdl–19.5) 0.1 (bdl–0.2) 10.6 (0.1–286.7) 0.1 (bdl–4.9) 7.4 (1.2–65.0) 20 250 (7–218500) 48 130	Groundwater Area B 7.1 (6.4–8.0) 3.8 (0.1–35.4) 30.5 (10.0–229.0) 4.1 (1–22.1) 0.1 (bdl–0.3) 0.8 (0.1–7.0) 0.1 (bdl–1.2) 5.1 (1.7–34.4) – 1524	Area C 7.2 (6.0–8.9) 1.0 (0.1–16.8) 11.2 (1.6–61.0) 0.3 (bdl-9.3 0.1 (bdl–0.4) 1.1 (0.1–119.3) – – 38 (3–870) 748	Leachate 8.2 (7.1–9.1) 698 (110–3480) 2928 (854–21219) 0.8 (0.1–15.1) 0.1 (bdl–2.9) 934 (233–2025) 0.1 (bdl–3.3) 876 (51–2933) 3080 (560–5670) 17 070	

Mean values and ranges of selected parameters and anion concentrations for surface water (M1–M4), groundwater (areas A–C), and leachate in the period of 1997–2011

Exceptions in measurements for particular parameters and sampling areas have been described in the text; ranges of values in parentheses; bdl – below detection limit.

Biochemical oxygen demand (BOD₅) and chemical oxygen demand (COD) are taken usually into consideration as main indices of the organic matter content, and in the case of presented data, they showed considerable variability (Table 1). The BOD_5 and COD values for surface water ranged from 0.7 to 246.5 and from 2.9 to 629.5 mg·dm⁻³, respectively; with the elevated values (over 100 and 200, respectively) detected in the years 2000-2002, and 2008. Both parameters did not display significant differences among the sampling sites, however, significantly lower values were observed in samples collected during spring time (Kruskal–Wallis, p < 0.05). The groundwater BOD₅ values did not exceed 65.0 mg \cdot dm⁻³, and the values were smaller for the samples from piezometers in area C. On the other hand, COD presented much higher values, especially in samples from piezometers localized close to the landfill (area A, piezometers C, P-2, P-3; up to 915.3 mg dm⁻³). Neither for BOD₅ and COD, nor for the other parameters, were any seasonal differences for groundwater samples observed. Moreover, no seasonal patterns were detected for the leachate samples, which presented highly elevated levels of BOD₅ and COD values, with a median value of 698 and 2928 $mg \cdot dm^{-3}$, respectively.

From all the investigated nitrogen compounds, ammonium nitrogen (NH₄⁺-N) concentrations displayed the highest variability in both types of water (Table 1). The coefficient of variation (*cv*) for the period average value ($5.1\pm21.8 \text{ mg} \cdot \text{dm}^{-3}$) in surface water samples was extremely high, equal to 424%, and this situation was caused by two elevated values detected at sites M3 and M4 (207.2 and 96.1 mg \cdot dm^{-3}, respectively) in 2008. For the remaining samples, ammonium concentrations did not exceed 30 mg \cdot dm^{-3}. Due to this variability, no significant differences were observed for ammonia among the Malinówka creek sampling sites (Kruskal–Wallis, p > 0.05). The concentrations of ammonia in ground water samples from area A were even higher, especially in piezometers P-2 and P-3, reaching 286.7 mg · dm^{-3}. In the remaining areas, ammonium concentrations did not exceed 10 mg · dm^{-3}, except for the samples from piezometer 22, where recorded values were elevated in the years 1997–2000. For leachates, ammonium values were frequently above 1000 mg · dm^{-3} (in 45% of all the samples), with a median value of 934 mg · dm^{-3}.

Nitrate concentrations generally did not exceed 5 mg·dm⁻³, except for the elevated values (6.2–15.1 mg·dm⁻³) observed in all of the Malinówka creek sites in 2007, and area A (P-3, P-6 and P-8) in 2009–2010 (5.8–19.5 mg·dm⁻³). Nitrite concentrations in surface water were mostly below 1 mg·dm⁻³ (Table 1). Values exceeding this level were detected in samples collected in all sites in June 2007. The nitrogen distribution pattern was followed by the phosphorous compounds, expressed as total phosphorous with an average value of 0.3 mg·dm⁻³ with cv = 145%. The maximum values, over 1 mg·dm⁻³, were detected in samples from 2007 and 2008. In the groundwater, nitrite concentrations did not exceed 0.5 mg·dm⁻³, and total phosphorous concentrations exceeding 1 mg·dm⁻³ were detected in samples collected from piezometers P-2 and P-3 in 2005 and 2010.

The mean total organic carbon concentration (TOC) in the surface water was at a level of $18\pm34 \text{ mg}\cdot\text{dm}^{-3}$, cv = 190%. Generally, values exceeding 15 mg $\cdot\text{dm}^{-3}$ were observed in site M4, however, the median value for this site was not significantly different from those in the other sampling sites (Kruskal–Wallis, p > 0.05). For the groundwater samples, the same level was exceeded in piezometer P-C (area A) and P-III-1 (area B). Leachates presented high variability of TOC values, with an average of 876 mg $\cdot\text{dm}^{-3}$ (Table 1).

While conductivity measurements were carried throughout the whole discussed period, chlorides were not investigated in surface and groundwaters until 2004 due to the changes in the regulations controlling monitoring effort around municipal landfills. In leachates, chlorides were investigated until 2010, with values in the range of 560–5 670 mg·dm⁻³. Surface water samples displayed extremely high concentrations of this ion, reaching almost 40 000 mg·dm⁻³ in 1998. Since 2002, chloride concentrations decreased to values lower than 3000 mg·dm⁻³. Among all the investigated sites, chloride concentrations were significantly low at site M1 (Kruskal–Wallis, p < 0.05). Conductivity values in the surface water samples in the whole investigated period (1997–2011) also displayed highly elevated levels, up to 94 000 μ S·cm⁻¹, and a highly statistical significant correlation has been observed (r^2 in the range of 0.88–0.98 for the particular sampling points) between both parameters. For the groundwater samples, both parameters displayed high values reaching 218 000 mg·dm⁻³ and 262 000 μ S·cm⁻¹. Such extreme values were observed in samples from area A, especially from piezometer P-3.

Table 2

Parameter	Surface water				
	M1	M2	M3	M4	
Cd	< 0.5-1.0	<0.5-2.9	<0.5-2.3	< 0.5-2.7	
Cu	< 0.004	<0.004-1.11	< 0.004	< 0.004	
Cr	< 0.01	< 0.01	< 0.01	< 0.01	
Hg	< 0.5	< 0.5	< 0.5	< 0.5	
Pb	< 0.01	< 0.01	< 0.01-0.02	< 0.01	
Zn	< 0.005-0.02	< 0.005-0.03	< 0.005-0.01	< 0.005-0.01	
Parameter		Th -+-			
	Area A	Area B	Area C	Leachate	
Cd	< 0.5	<0.5-49.0	< 0.5	< 0.5-3.1	
Cu	< 0.004-0.21	< 0.004-0.06	< 0.004-0.01	< 0.004-2.3	
Cr	< 0.01	< 0.01	-	< 0.01	
Hg	< 0.5-0.95	< 0.5		< 0.5	
Pb	< 0.01 - 3.17	< 0.01-0.2	< 0.01	< 0.01-0.34	
7n	<0.005-3.00	<0.005-0.19	<0.005-0.03	<0.005-0.85	

Heavy metal concentrations in surface water (M1–M4), groundwater (areas A–C), and leachate in 1997–2011

In parentheses, ranges of values are given; bdl - below detection limit.

Heavy metal concentrations (Cd, Cu, Cr, Hg, Pb, and Zn) in the all investigated surface and groundwater samples (Table 2) were generally well below the standards adopted by the water Framework Directive as threshold values for class I surface water quality, except for the single exceedances for cadmium and copper in 2007. Elevated concentrations of Cd, Cu, Pb, and Zn were sporadically observed in the leachate samples. For the period 1997–2002, other element concentrations (B, F, Ca, Na, K, Mg, Mn) were investigated in leachates and groundwater from piezometers localized in areas A and C. Collected groundwater samples displayed extremely high concentrations of Ca, Na, and Mg (up to 6466, 107 700, and 2356 g·dm⁻³, respectively) which was followed by high values of the hardness parameter, up to 21,163 mgaCO₃·dm⁻³. Whereas concentrations in leachates were at a much more lower level, only up to 363, 1,719, and 458 mg·dm⁻³, for Ca, Na, and Mg, respectively.

4. DISCUSSION

General leachate parameters for the Barycz landfill match the data for municipal landfills presented in the literature, except for chlorides and conductivity, which were slightly above reported levels [1-2, 12]. Since, samples were collected only in one site, where leachates from the different landfill stages are already mixed, it should be assumed that they represent the average quality of leachate for this facility. No significant seasonal or temporal trends have been detected in the leachate measurement dataset (Kruskal–Wallis, p > 0.05). Furthermore, the wide range of the BOD₅/COD ratio (0.02-0.80), which is considered a measure of biodegradability, did not show any temporal pattern, and could not be related to the age of the landfill [13]. However, in the case of the presented monitoring data, the COD values should be treated with particular attention, especially for samples with high salinity. COD during laboratory analyses has been determined with the use of potassium dichromate as an oxidizing agent, and not corrected with the use of mercuric sulfate to eliminate the chloride interference [14]. A strong and statistically significant correlation for the available datasets (r^2 between 0.69 and 0.88) confirms that the COD values are likely skewed in the presence of chlorides. Hence, the subsequent discussion puts the stress on its distribution, not on the range of values. Since, TOC concentration was determined using catalytic combustion, followed by infrared spectrophotometry, it was assumed that the high salinity of samples did not alter the TOC measurements.

Parameters usually discussed in the case of landfill impacts on the aquatic environment (i.e., BOD_5 , NH_4^+ -N, TOC) indeed demonstrated elevated values at the Malinówka creek sampling sites, especially at site M3 localized directly downstream from the facility. This trend has been previously reported in the area [9, 15]. Average concentrations of BOD_5 detected in a site upstream from the landfill (M1) were not significantly, or even noticeably lower from the values observed at sites M2 and M3 (Fig. 2).



Fig. 2. Temporal distribution of average BOD₅ in groundwater (areas A–C), surface water (M1–M4), and leachate



Fig. 3. Temporal distribution of average NH¹₄N concetration in groundwater (areas A–C), surface water (M1–M4), and leachate

A similar trend was observed for NH_4^+ -N values in 2005–2007 (Fig. 3). This indicates that the Malinówka creek, upstream from the landfill, carries contamination originating from the upper part of the catchment, which is likely due to the surface runoff source which contributes to the overall contamination level of this creek. As for the site localized 1 km downstream from the landfill (M4), the same parameters were generally not detected at a considerably lower level, which could signify a decrease in the landfill impact at this site. However, the anthropogenic impact at the downstream part of the catchment should also be highly noted. The quality of surface water at site M4 is also possibly affected by the surface runoff from agriculture areas which are responsible for the elevated TOC level at this site. It should also be noticed that discussion on the significant differences between the site data series has been hindered due to the high variability of measured parameters. Such variability is typical of surface running waters due to natural reasons. The average precipitation (1997–2011) at the local gauge station (Koźmice Wielkie, IMGW) with the yearly value of 4.3 ± 7.3 mm, showed an increase and high variability from May through September (monthly averages from 6.0 ± 8.0 to 8.0 ± 11.7 mm) which supports observations about decrease of concentrations during spring/summer measurements, when creek flows are elevated due to rainfalls.

As for groundwater samples, noticeably high concentrations of all parameters were detected in area A, especially in piezometers localized close to the landfill (C, P-2, P-3). The average values for areas B and C were substantially lower in the respective time periods, as presented by BOD₅ and NH₄⁺-N (Figs. 2 and 3). This demonstrates that the direct impact of the landfill on the groundwater is limited to the direct proximity of the facility (area A). It should also be noted that the average concentrations of the investigated parameters for area A were significantly lower than the values measured in leachate (Kruskal–Wallis, p < 0.05). As for the relationship with the parameters in the Malinówka creek sampling sites, no significant differences have been observed due to data variability, though the average values were at a similar level, as for sites M3 and M4.



Fig. 4. Temporal distribution of average conductivity values in groundwater (area A), surface water (M1 and M3), and leachate

Despite the presence of the landfill and the noticeable surface runoff impact, the most distinctive issue for the aquatic environment in this area is the chloride contamination. Since, chloride measurements have been suspended during the monitoring effort, the subsequent discussion is based on conductivity distribution. Conductivity observed in the leachates was within, or only slightly above, the limits presented for various landfills [1, 2], and noticeably higher than the values noted in the Malinówka creek samples (Fig. 4). The average level of conductivity of the surface waters exceeded the EU guideline values established for surface water (309 μ S·cm⁻¹ for class II, watercourse type 12, [16]), especially in 1998 and 2001. However, it should also be noted that after these two events, the conductivity in surface water decreased and remained at the guideline levels (except for 2008). An extremely high conductivity was observed in groundwater samples collected in area A, with an average value of 66 523 \pm 65 297 μ S cm⁻¹. The reason behind such extreme salinity of the samples collected from the piezometers in area A is clearly the localization of the landfill. As mentioned before, the Barycz landfill occupies the former salt mine area, mainly natural hollows and depressions resulting from surface subsidence commonly occurring due to the mining of salt [17, 18]. The weight of the deposited waste load causes an extrusion of brine filling the caverns left after rock salt excavation, which due to the permeability of formations, comes into contact with the aquifer (the presumed groundwater flow directions are presented in Fig. 1). Since, brine flow outside the deposit boundaries is not very likely, due to the presence of poorly permeable and impermeable formations in the landfill neighborhood, the conductivity of groundwater in areas B and C were expected to be at a much lower level. Indeed, the average conductivity in these areas was similar to that observed in the Malinówka creek, and below the EU guidelines values established for ground water (3000 μ S·cm⁻¹ for class V [19]). The graphic presentation of conductivity measurements in all the media (Fig. 4) also displays an intermittent character of brine extrusions which are visibly reflected in changes of conductivity in all the investigated media. An explicit separation of the chlorides impact from the landfill and the brine is not possible, especially since the two first stages of the landfill were built without sealing the landfill base. The entire dataset shows however, that the chloride contamination has been declining since discontinuation of the salt excavation.

5. CONCLUSIONS

The dataset from a 15-year period from the Barycz landfill monitoring network provides an insight into the sources of surface and groundwater contamination. Parameters characterizing the landfill impact on the aquatic environment demonstrated elevated values at the Malinówka creek sampling sites, especially at sites localized directly downstream from the facility. However, detailed assessment of the extent of this impact has been hindered due to overlapping anthropogenic and natural factors. The multiple sources of possible wastewater contamination in the catchment, and hydrological settings based on the former mining area, equally influenced the chemistry of surface water in this area. The direct impact for the groundwater is visible, but limited to the direct proximity of the facility. Nevertheless, the presumed directions of infiltration water and groundwater flow indicate a potential mixing zone of rainwater, shallow groundwater, and landfill leachate. The hydrogeologic settings of the landfill induce though the most evident evolution of surface and groundwater chemical composition. The brine extrusions from the salt formations, due to the growing weight of the waste collected in the landfill, caused the extreme chloride concentrations, and following conductivity level. The long-term monitoring effort illustrates however, that the conductivity has been declining since discontinuation of the salt excavation, however, this depends greatly on the actual hydrogeological conditions in the salt mine.

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