

Article

Levels of Organic Pollution Indicators in Groundwater at the Old Landfill and Waste Management Site

Eugeniusz Koda, Anna Miskowska and Anna Sieczka *

Department of Geotechnical Engineering, Faculty of Civil and Environmental Engineering, Warsaw University of Life Sciences, Nowoursynowska 159 St., 02-776 Warsaw, Poland; eugeniusz_koda@sggw.pl (E.K.); anna_miskowska@sggw.pl (A.M.)

* Correspondence: anna_sieczka@sggw.pl; Tel.: +48-22-593-5222

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Abstract: The aim of this paper was to assess groundwater quality in a landfill and waste management site, with special regard to levels of organic pollution indicators: chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total organic carbon (TOC). Analysis of specific indicators was conducted for piezometers located in the area of the Radiowo landfill, the composting plant and the facilities adjacent to the landfill. The article discusses the temporal and spatial changes of selected organic pollution indicators. Based on the results of groundwater monitoring, several maps of COD, BOD and TOC areal distribution were provided. Statistical distribution of monitoring data was presented using box-and-whisker plots. Pearson's correlation coefficients between selected pollution indicators were measured with a significance level set at $p < 0.01$ and $p < 0.05$. The strongest correlation was observed between BOD and COD. The maximum BOD/COD ratio was observed at the level of 1.561 before the closure of the vertical barrier, whereas, at present, average values of this ratio are below 0.18. The results indicate significant improvement of groundwater quality in the landfill site after the closure of the vertical barrier. In particular, this refers to BOD values, which decreased even 160 times in the 1998–2016 monitoring period.

Keywords: landfill; pollution; monitoring; biochemical oxygen demand; chemical oxygen demand; total organic carbon

1. Introduction

Nowadays, landfilling is the most common practice of waste disposal all over the world [1,2]. In 2015, a total of 10.9 million tons of municipal solid wastes were collected in Poland, of which 44.3% were landfilled in 347 operating landfills [3].

Landfill leachate is considered the main source of groundwater and surface water contamination. In recent decades, the influence of leachates on water resources has attracted a lot of attention because of its high environmental significance [4,5]. Leachates mainly contain immense amounts of organic matter, ammonium, heavy metals, and salts [6–8]. According to Christensen et al. [1], the components of leachates can be subdivided into the following groups: organic matter expressed as chemical oxygen demand (COD) and total organic carbon (TOC), specific organic compounds, inorganic compounds, and heavy metals. Leachates are commonly characterized by high chemical and biochemical oxygen demand values (COD and BOD, respectively) that reflect concentrations of soluble organic matter. The organic composition of leachates is variable depending on the characteristics of the landfilled wastes, age of the landfill or climatic conditions [8,9].

In order to protect the natural environment from leachates, each landfill must be properly secured, for example by using artificial sealing based on cohesive soil liners [8]. Municipal landfills contain a high content of organic wastes, with great impact on the biogeochemical processes in the landfill body and leachate generation with a substantial content of ammonium, dissolved organic carbon and organic compounds [9].

It is important to stress that the content of organic matter affects the level of dissolved oxygen and can be determined by measurements of the biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The BOD is also used as a value to indicate the leachate “quality”.

In cases when leachate is discharged directly into a watercourse, it will absorb oxygen from the water to complete its decomposition. As a result, the level of oxygen in water may fall below a minimum supporting aquatic life [10].

Because of the decomposition of organic matter, leachate derived from landfills comprises primarily dissolved organic carbon [11]. The solubility of organic contaminants in wastes can be slightly enhanced through the presence of high levels of organic carbon in the leachate [12].

The composition of landfill leachate varies over time. Leachates generated during the early stages of anaerobic degradation are characterized e.g., by high BOD values and a high BOD/COD ratio. According to Getinby [13], BOD values are the highest in the first five years of landfill operation and decrease with time (for example BOD equal to 2000 mg O₂/L after five years and BOD equal to 70 mg O₂/L after 40 years of landfill operation). Similarly, five-year leachates are characterized by a COD value at a level of 8000 mg O₂/L, but, after 30 years, this value decreases to 500 mg O₂/L.

BOD and COD indicators have a significant meaning in environmental studies because of their ability to indicate the pollutant strength of polluted water [14,15].

In recent years, the impact of landfills on groundwater quality has enhanced numerous studies relating to the assessment of the soil-water environment near landfills and waste management facilities [6,16–24].

Owing to the fact that groundwater quality within the landfill site should be controlled by a monitoring system based on a network of piezometric wells and sampling points located along surface streams near the landfills, this study focuses on detailed analyses using data from a monitoring period of almost 20 years (1998–2016).

The principal aim of this paper is to evaluate the impact of the landfill and the waste management facilities on the groundwater quality within the landfill site. With particular emphasis on the extent of groundwater contamination by organic substances, concentrations of BOD, COD and TOC were determined in the collected samples. This can complete and add additional information to Radiowo landfill monitoring data results which have been published [21]. An attempt was also made to answer the following questions: (1) “Is groundwater quality significantly affected by leachate percolation from the landfill?” (2) “Does a vertical barrier limit the spread of pollutants to the soil-water environment?”

2. Materials and Methods

2.1. Site Characteristics

The Radiowo Landfill (52°16′47.80″ N, 20°52′45.30″ E) is located partly in the Stare Babice commune and partly in Warsaw, the capital of Poland (Figure 1). It covers an area of ca. 16.2 ha and its elevation is almost 60 m. From the north, the landfill lies adjacent to a composting plant and a waste treatment plant located in the Warsaw–Bielany District.

A Mechanical-Biological Treatment (MBT) installation located in the study area was built in 2012–2014 as a result of the reconstruction of the former compost plant, which operated on the DANO technology. The area of the MBT installation covers almost 10 ha. The composting plant is situated on the western side from the railway siding and since 2013 has been working as an element of the Regional Municipal Waste Treatment Installation. The basic role of this installation is the production of a stabilat, which contains a reduced content of organic fraction and can be disposed on non-hazardous

and inert waste landfills. The capacity of this installation, measured as the mass of mixed processed wastes, is approximately 1000 tons per day. From the south and east, the landfill is surrounded by the Forest Park “Bemowo” and two Nature Reserves (Kalinowa Łąka and Łosiowe Błota). To the west occurs a railway siding, and industrial and service facilities. A paved storage yard is located ca. 200 m from the toe of the landfill slope, and to the northwest lies a fuel storage base. The Zaborowski Canal watercourse (connected with the Lipkowska Woda stream) occurs to the north from the landfill, at a distance of about 350 m from the composting plant (400 m from the landfill). The area of the Kampinos National Park is situated approximately 3 km to the northwest of the Radiowo landfill [21].

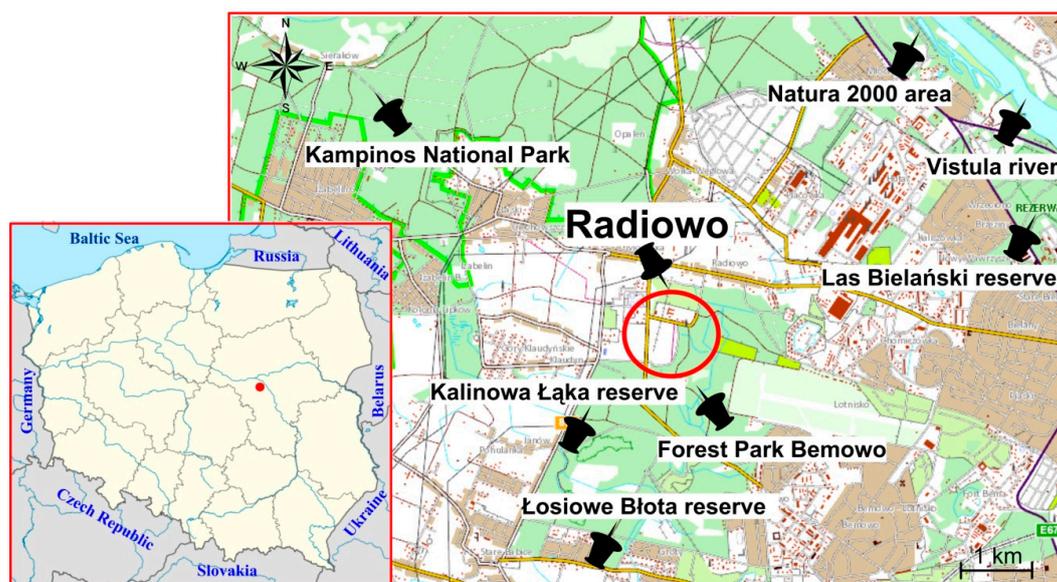


Figure 1. Location of the study area in relation to protected areas.

From 1962 to 1991, the Radiowo landfill was a disposal site for the municipal wastes from Warsaw. Since 1992, only non-composted wastes from the Radiowo compostory plant are stored on the landfill, and, since 2012, only waste from the MBT installation is stored there. Since 1994, remedial works have been carried out on the landfill site, including forming and planting of slopes, reinforcement of their stability, clay mineral capping, construction of a bentonite cut-off wall, peripheral drainage, and installation of a leachate re-circulation system.

A vertical barrier was designed to minimize the spread of pollutants to the groundwater system. This construction provides favorable hydraulic conditions by forcing a lowered groundwater level inside the peripheral cut-off wall in relation to the natural water level around the landfill site [25].

2.2. Geological and Hydrogeological Conditions

The landfill subsoil consists of sandy soils with a thickness of 2–15 m. The upper part is represented by dense sands underlain by well-graded sands. The first groundwater level is at the depth 0.3–2 m below the surface level and its fluctuations depend on the weather and the local drainage conditions.

The deeper part of the subsoil consists of low permeable boulder and varved clays (thickness 25–40 m, average permeability coefficient at 10^{-9} m/s). Drillings have revealed the occurrence of fluvio-glacial sands on the south and southwestern side of the vertical barrier, and boulder clays in the remaining sections of the barrier. These deposits occur on glaciotectonic landforms composed of Pliocene clays. Due to the differentiation of soils occurring in the soil profile, the subsoil can be subdivided into five geotechnical layers (Table 1).

Table 1. Main geotechnical characteristics of the subsoil.

Layer	Soil	I_L or I_D	Stratigraphy	ρ	k
I	clSa	0.4	Quaternary (Pleistocene)	2.1	9.2×10^{-6}
II	Sa	0.7	Quaternary (Pleistocene)	2.0	5×10^{-5}
III	saclSi/Cl	0.2	Quaternary (Pleistocene)	2.1	1.2×10^{-7}
IV	saCl	0.1	Quaternary (Pleistocene)	2.2	3×10^{-8}
V	Cl/saCl	<0.25	Tertiary (Pliocene)	2.1	$<10^{-9}$

Notes: I_L : liquidity index (-), I_D : density index (-), ρ : bulk density of soil (g/cm^3), k : coefficient of permeability (m/s).

The groundwater flow direction is from the southeast to the northwest. Nevertheless, changes in groundwater levels, the presence of drainage systems and linear embankments, surface development, and the shape of the landfill force local changes of the flow direction. Low hydraulic gradients in the southern and eastern part of the area adjacent to the landfill result in very low velocity of the groundwater flow (inflow to the landfill). The influence of the vertical bentonite barrier on the groundwater flow was modeled in our previous studies using the numerical modeling techniques [26]. The FEMWATER model, using 3D finite elements method, was used to solve the issue of groundwater flow described by Richard’s equation. According to that modeling studies, it was noticed the groundwater level increase from approximately 0.25 m in the southern part to more than 0.75 m in the north-western part of the landfill site. Small increase (ca. 0.2 m) of the groundwater level was observed in the area close to the south part of the landfill.

Flow velocity on the western side of the landfill (beyond the railway siding) is significantly higher. Along the outflow direction from the landfill, the velocity of groundwater flow in sandy soils is about $5.8 \times 10^{-7} \text{ m/s}$ (for a hydraulic gradient at $i = 10\%$), but this value, as mentioned above, may undergo changes depending on the flow direction, and the hydrogeological and meteorological factors.

2.3. Technical Characteristics of the Vertical Barrier

The 0.6 m wide vertical barrier was installed at a depth of 2 m below the top of the clayey soils, at an average level of 3.5–22 m below the surface, which had resulted from the variable depths with regard to the top of the impermeable layer. The permeability coefficient for the cut-off wall is below 10^{-9} m/s [19], making the subsoil environment practically impermeable. The characteristics of the vertical barrier are presented in Table 2.

Table 2. Characteristics of the vertical barrier.

Parameter	Unit	Value
Geometric Parameters		
Thickness	m	0.6
Length	m	1687.2
Minimum depth	m	3.0
Mean depth	m	8.6
Maximum depth	m	22.0
Lateral surface area	m^2	14529.8
Filtration Parameters		
Permeability coefficient after 28 days	m/s	2.5×10^{-8}
Permeability coefficient after 60 days	m/s	1.0×10^{-9}
Strength Parameters		
Compressive strength after 28 days	MPa	min. 0.53
Compressive strength after 60 days	MPa	min. 0.91

2.4. Monitoring Network

The monitoring system of the landfill site includes three basic elements: (1) groundwater; (2) surface water; and (3) leachates. Shallow piezometers and one deep well were installed in the

landfill site in order to control groundwater quality (Figure 2). Moreover, three sampling points were selected along the Lipkowska Woda watercourse to monitor surface water quality.

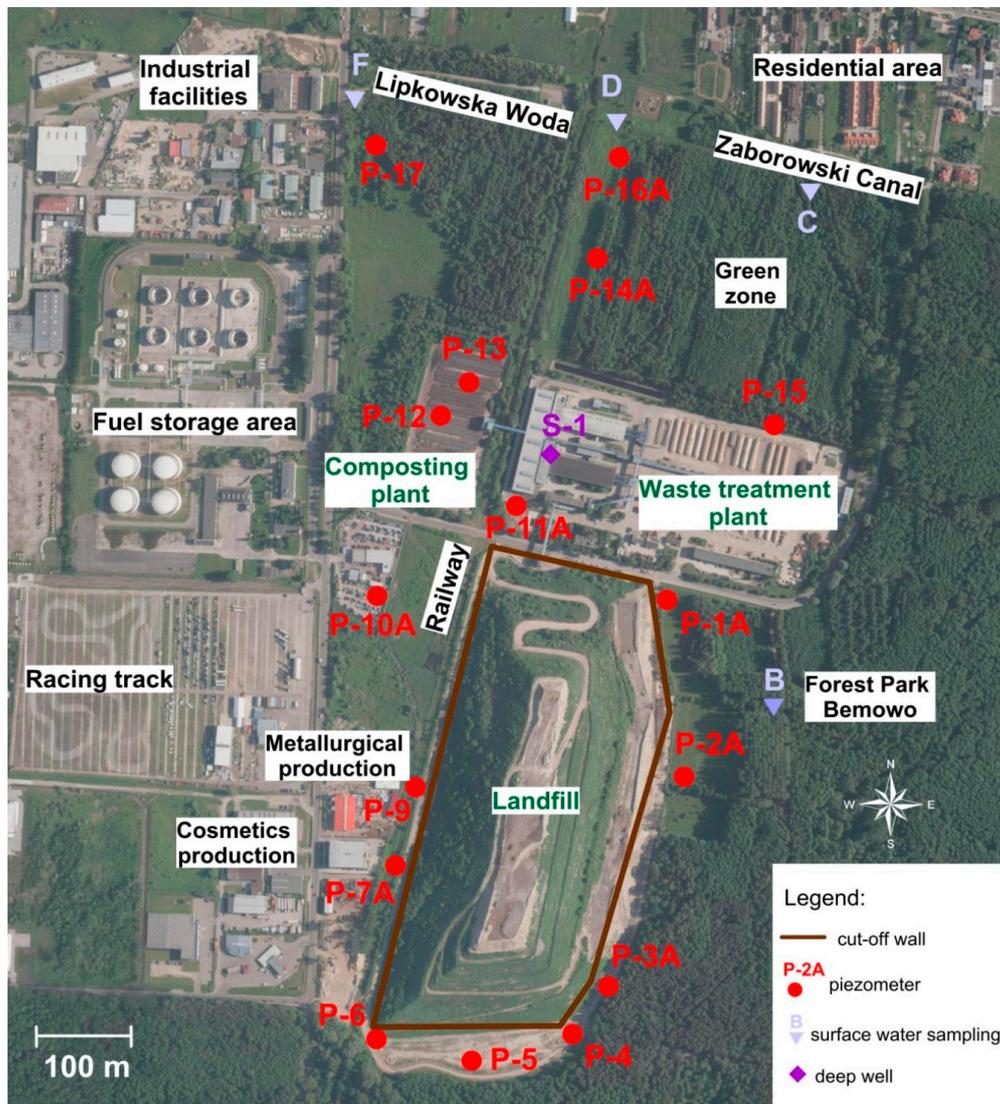


Figure 2. Location of the groundwater monitoring network in the study area.

Leachates were monitored in three sampling points in order to examine the amount of generated leachate and its quality. Fifteen indicators of pollution were examined for the leachates, surface water and groundwater.

Quality tests were carried out focusing on the following indicators: electrical conductivity (EC), pH, lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), chromium (Cr), mercury (Hg), total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAH), ammonium (NH_4^+), chemical oxygen demand (COD), biochemical oxygen demand (BOD), chlorides and sulfates.

Moreover, continuous measurements of the precipitation and groundwater level were carried out as part of monitoring program for the landfill. The average value of a rainfall for analyzed area is 550 mm. Groundwater level in all piezometers shows seasonal pattern resulting from precipitation. It is also observed that due to the high groundwater level, lower concentration of pollution indicators is noted and conversely. Therefore, the physicochemical analyses of the groundwater samples can be coupled with measurements of groundwater level changes in piezometers.

The monitoring network of the Radiowo landfill consists of: piezometer P-2A located on the outflow, to the east of the landfill; piezometers P-4 and P-6 located on the inflow (background), to the southeast of the landfill; piezometers P-7A, P-9, P-10A, P-11A, P-12 and P-17 located in the outflow; piezometers P-14A and P-15 located in the outflow, to the north from the composting area; and deep well S-1 located in the compostory plant area. Monitoring studies are conducted quarterly and annual reports are submitted to the administrative bodies responsible for the environment-related issues.

2.5. Sampling and Experimental Analysis

Owing to the fact that about 30% of the monitoring results may be biased due to inappropriate sampling and sample transportation [27], all samples were collected with great care to eliminate potential errors. Water samples were collected in accordance with the procedure outlined in EN ISO 5667-3 [28] and ISO 5667-11 [29]. Before sampling, the top water in each piezometer was carefully pumped out. Calculations of the pumping time were based on the volume of water in each piezometer and the pump efficiency. To assure sampling appropriateness, each pumping was accompanied with simultaneous measurements of pH, temperature and electrical conductivity. Groundwater samples were taken four times in each year (March, June, September and November).

Chemical analysis of COD, BOD and TOC were conducted according to PN-ISO 15705:2005P [30], PN-EN 1899-2:2002P [31] and PN-EN 1484:1999P [32], respectively. Additionally, the values of pH and EC were measured in accordance with the recommendations presented in PN-EN ISO 10523:2012 [33] and PN-EN 27888:1999 [34].

Analysis of changes of the pollution indicators was carried out in a temporal and spatial aspect. Graphs of BOD, COD and TOC concentrations were presented for piezometers located in the landfill area, composting plant, and the adjacent service facilities. The obtained results were compared with the groundwater quality standard presented in the Regulation of the Minister of the Environment of Poland [35] (third class representing good groundwater quality).

2.6. Statistical Analysis

The monitoring data were analyzed using the Statistica 12.0 software package. Pearson's correlation coefficients (r) were calculated between each of the pollution indicator levels in groundwater, with a significance level set at $p < 0.05$ and $p < 0.01$. The purpose of the statistical analysis was to present the existing correlations between pollution indicators with respect to the specific locations of piezometers from which the groundwater samples were taken. In order to display the entire statistics of the dataset, box-and-whisker plots were used. The minimum, quartile 1 (25%), median, mean, quartile 3 (75%), and the maximum values were determined.

3. Results

3.1. Pollution Level in Groundwater Due to Localization of Piezometers

Based on the monitoring studies, the most vulnerable to contamination were the areas closest to the landfill (0.5 km zone), mainly to the northwest and southwest. Monitoring results from piezometer P-2A, located at the outflow on the eastern slope of the landfill, indicate significant changes in the levels of pollution indicators, in particular caused by organic waste storage. Slight increase of the TOC level observed in this piezometer may be a result of its localization in a forest area. A similar trend in the TOC level, caused by forest surroundings, was also noted in piezometer P-4.

Monitoring results from piezometer P-6A, localized in a local depression with periodically stagnant water on the surface, show pollution concentrations exceeding the acceptable values for the third water quality class. Exceeded values primarily refer to the TOC level, which can be regarded as typical of a forest area.

For piezometer P-7A, the most visible changes concern the COD level. Exceeded values of this parameter result from its localization in an overgrown area.

A similar trend in the COD level changes is observed for the monitoring results from piezometer P-9, which is very much dependent on the putrefaction of vegetal remnants along the railway siding situated near to this piezometer. In the case of piezometer P-9, the fluctuations of some pollutant concentrations (for example the TOC level) also result from its localization. Particular influence on the concentration of selected pollution indicators has the nearest area where the production and service facilities are situated.

Higher concentration levels of contaminants in piezometer P-11A result from a local depression where the piezometer is located. Because of this, water from the railway siding and the composting area can flow down easily to that point and directly cause groundwater pollution in this piezometer.

Fluctuations in the concentrations of pollution indicators (especially TOC) and exceeded standards for the third class of groundwater quality were also observed in piezometer P-12. The main reason for this is runoff of contaminants from the composting plant area.

Groundwater in piezometer P-14A meets the standards for the third class of water quality. Only periodic fluctuations in TOC and COD concentrations may result from seasonal changes of groundwater level, which means that increased values of these parameters correspond to lower groundwater levels.

Apart from the sporadic excesses above reference values, the TOC and COD concentrations in groundwater from piezometer P-15 located in the area of the MBT installation comply with Polish standards. Seasonal fluctuations of these indicators can be attributed to runoff from the compostory plant and seasonal changes of groundwater level.

Seasonal changes in pollution indicator levels observed in groundwater from piezometer P-17 are determined mainly by runoff of contaminants from Estrady St. and the industrial facilities located nearby.

Based on the obtained results, it can be concluded that the concentrations of the analyzed parameters have decreased with the distance from the landfill, which can be linked to biodegradation and dilution.

A similar trend proving that concentrations of contaminants in groundwater decrease with increased distance from the pollution source was presented by Ling and Zhang [23], Aderemi et al. [36] and Mor et al. [37].

Regarding the influence of precipitation on contaminant concentration we can also claim that the concentrations are linked to the groundwater level which is mainly supplied by rainfall. According to groundwater level monitoring data (not presented in this article) it is noted that groundwater level in all piezometers show seasonal pattern. It should be noted that in accordance to high precipitation and resulting from this high groundwater level, lower concentration of indicators are observed.

3.2. Areal Distribution and Temporal Changes of Organic Pollution Indicators (BOD, COD, TOC) in Groundwater

3.2.1. Biochemical Oxygen Demand (BOD) in Groundwater

As presented by Hazelton and Murphy [38], typical BOD values are: 150–300 mg O₂/L for raw sewage, 200–600 mg O₂/L for storm water runoff from residential areas, and 20–30 mg O₂/L for treated sewage. Unpolluted natural waters are characterized by BOD values below 5 mg O₂/L. It can also be stated that a BOD level between 1 and 2 mg O₂/L indicates very clean water, 3.0 to 5.0 mg O₂/L indicates moderately clean water and BOD > 5 mg O₂/L indicates a nearby pollution source. At BOD levels of 100 mg O₂/L or higher, the water supply is considered as very polluted with organic waste.

Monitoring data of BOD in groundwater show that two years before the closure of the vertical barrier, the BOD values exceeded 500 mg O₂/L in some parts of the monitored area (Figure 3). Such high concentrations referred to the western and northern part of the landfill site, strictly surrounding piezometers P-9, P-7 and P-11A. In the eastern part of the study area, the BOD concentrations were in the range of 100–260 mg O₂/L. As a result, it can definitely be stated that a large part of the study area was at that time contaminated by organic compounds.

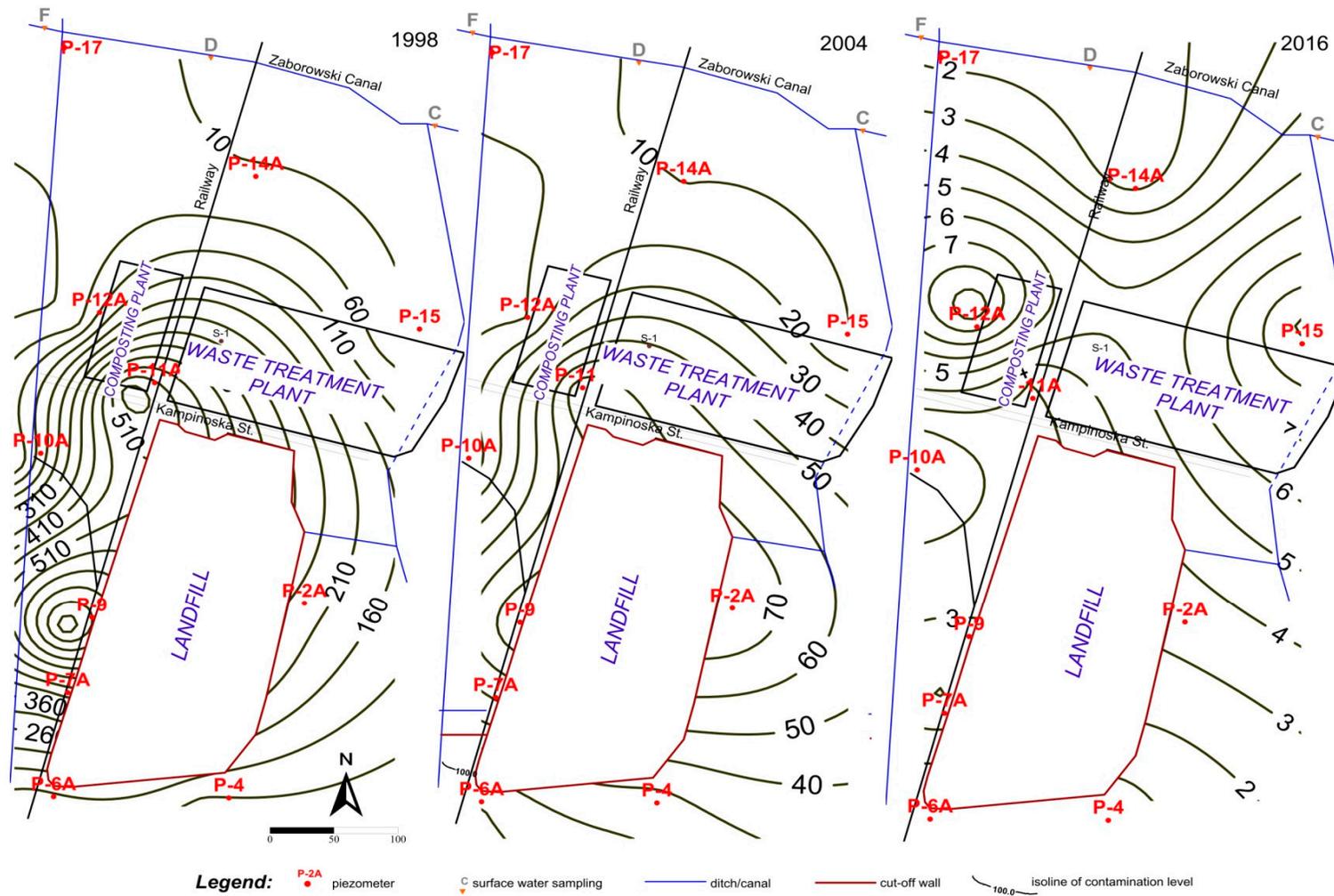


Figure 3. Distribution of the mean values of the biochemical oxygen demand (BOD) in groundwater in 1998, 2004 and 2016.

Worth emphasizing is the fact that, as compared to the survey outcomes from 1998, BOD concentrations were even seven times lower four years after the closure of the vertical barrier (2004). The highest concentrations of BOD recorded at that time in the monitored area did not exceed 70 mg O₂/L, but still referred to the presence of organic contaminants in groundwater (Figure 3).

For actual monitoring data (2016), the results show a low BOD level (1.0–7.0 mg O₂/L), which means that groundwater has not been contaminated with fresh leachate. Increased values of BOD (6–7 mg O₂/L) concentrations were measured only in the area of the composting plant and the MBT installation.

Similar results reporting low BOD concentrations in piezometers located at the landfill site were reported, for instance, by Ngang and Agbazue [15], Bandara and Hettiaratchi [39], and Sugirtharan and Rajendran [40]. As opposed to these examples, incomparably higher values of BOD were recorded at a municipal solid waste landfill site in Sri Lanka (BOD = 3590 mg O₂/L) [41].

Additionally, valuable is observation of temporal changes of the BOD level from 1998 to 2016 (Figures 4–6). Apart from the changes before the closure of the vertical barrier (November 2000), the monitoring data show stabilization with some exceptions in case of piezometers located in the area of adjacent facilities. However, in piezometers P-10, P-17 and P-14, data show very low values so even some changes are acceptable and should not be disquieting. It is also worth emphasizing that changes of pH can affect the microorganisms that consume the organic matter and then affect the level of pollution caused by organic compounds. The microorganisms (their amount and activity) have the significant impact on BOD values. In the case, when the amount of microorganisms is small, the processes of biochemical breakdown do not occur or intensity of the biochemical breakdown is insignificant. In natural conditions, such effect is often caused by the presence of toxic compounds (e.g., heavy metals) that adversely affect the enzymatic activity of the microorganisms. In that case, it must be considered that the changed values of BOD do not reflect the actual level of water pollution.

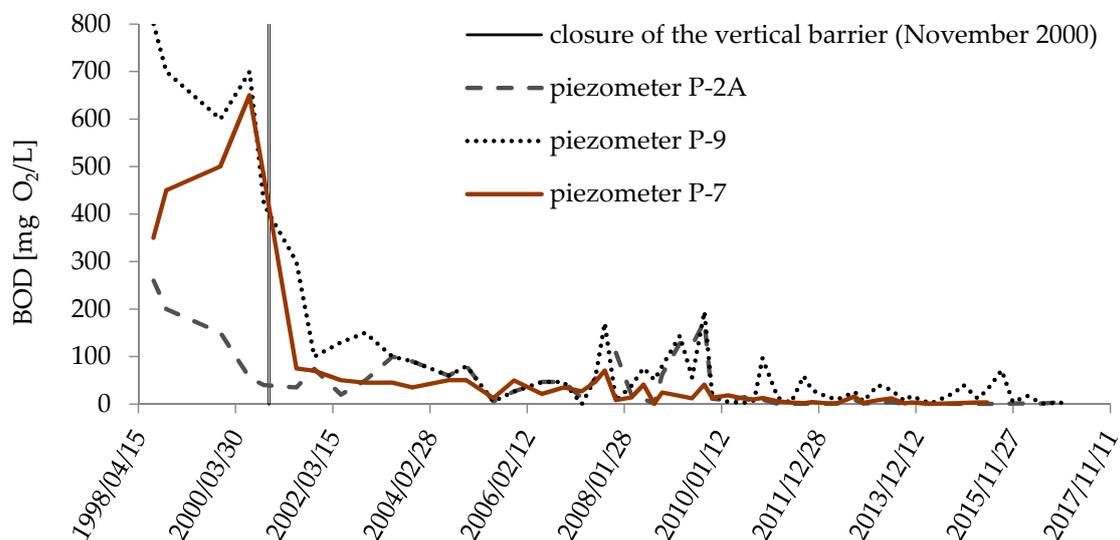


Figure 4. Temporal changes of the BOD level in piezometers located in the landfill area.

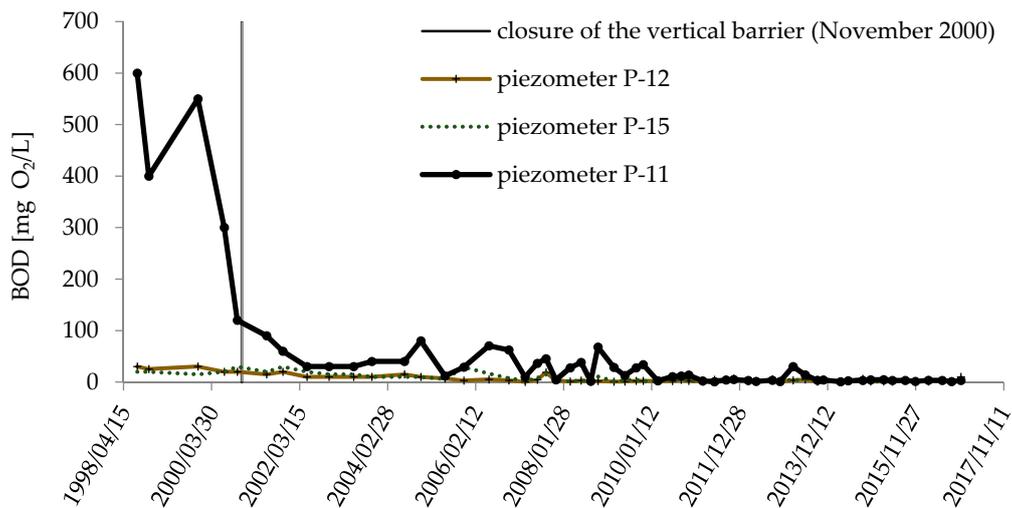


Figure 5. Temporal changes of the BOD level in piezometers located in the area of composting plant.

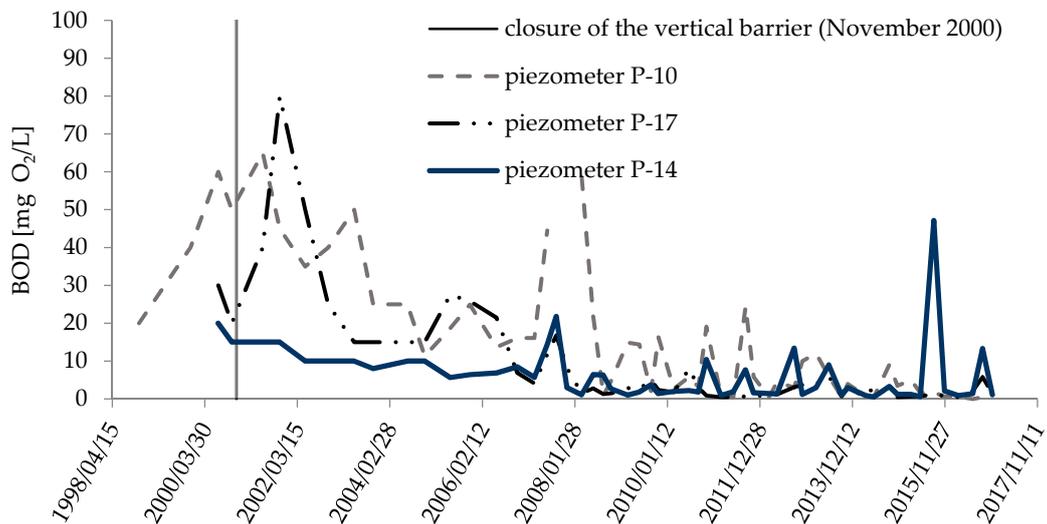


Figure 6. Temporal changes of the BOD level in piezometers located in the area of adjacent facilities.

3.2.2. Chemical Oxygen Demand (COD) in Groundwater

In this study, the chemical oxygen demand (COD) was used for assessing organic pollution levels in groundwater (Figure 7). Based on the monitoring results from 1998, it should be noted that the highest COD level was observed near piezometer P-7A (COD value at 700 mg O₂/L). Lower COD values were obtained for groundwater taken from piezometers located in the northern part of the study area, beyond the area of the MBT installation and the composting plant. In piezometers located in the area of the biological processing of wastes, average values of COD were in the range of 100–150 mg O₂/L. In the eastern and western part of the study area (vicinity of piezometer P-2A and P-9, respectively), the COD level was almost equal to 400 mg O₂/L. The lowest level of COD was detected in the northern part of the study area (COD at the level of 10 mg O₂/L). Monitoring data from 2004 and 2016 clearly indicate a decrease of COD concentrations in the piezometers. The most significant change had occurred near piezometer P-7A (COD level decreased from 703 mg O₂/L in 1998 to 132 mg O₂/L in 2004 and 100 mg O₂/L in 2016).

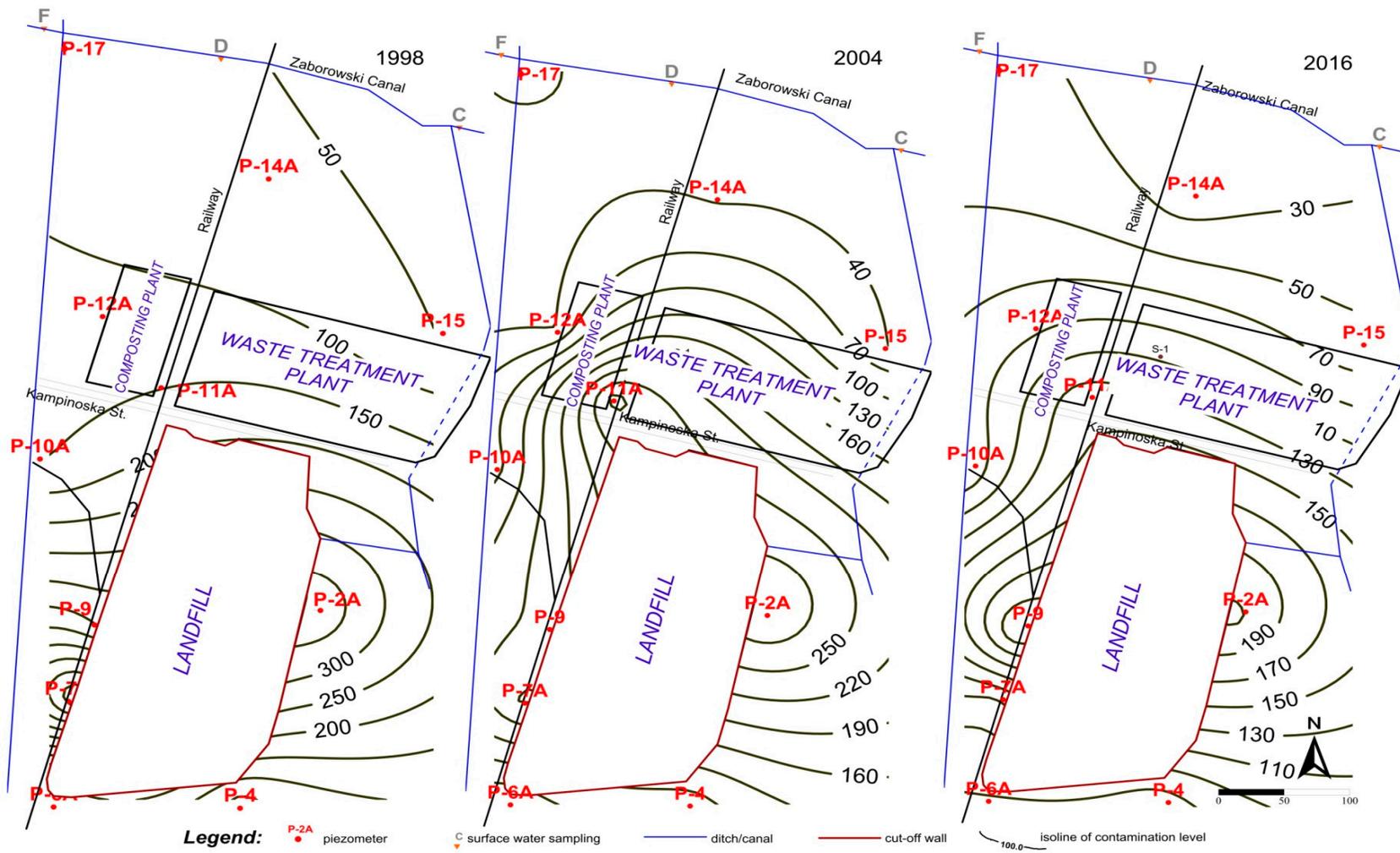


Figure 7. Distribution of the mean values of the chemical oxygen demand (COD) in groundwater in 1998, 2004 and 2016.

Figures 8–10 show stabilization in the COD level after November 2000 in almost all piezometers with the exception of piezometers P-9, P-11 and P-10. In piezometer P-9, located in the area of landfill, the most visible change in COD level has been observed after 2006. It depends on the putrefaction of vegetal remnants along the railway siding. In piezometer P-11, located in the area of composting plant, significant increase of COD level was observed in 2005, 2009 and 2012. Apart from these changes, monitoring data show stabilization. There is no doubt that development of an adjacent area is the main cause of COD changes in groundwater in piezometer P-10.

In Poland, there are no standards established for the COD level in groundwater or water intended for human consumption, but general standards for discharge of environmental pollutants mention the value of COD equal to 250 mg O₂/L as the highest acceptable limit. For instance, according to the National Agency for Food and Drugs Administration and Control (NAFDAC), the recommended maximum permissible level of COD is given as 294 mg O₂/L [42].

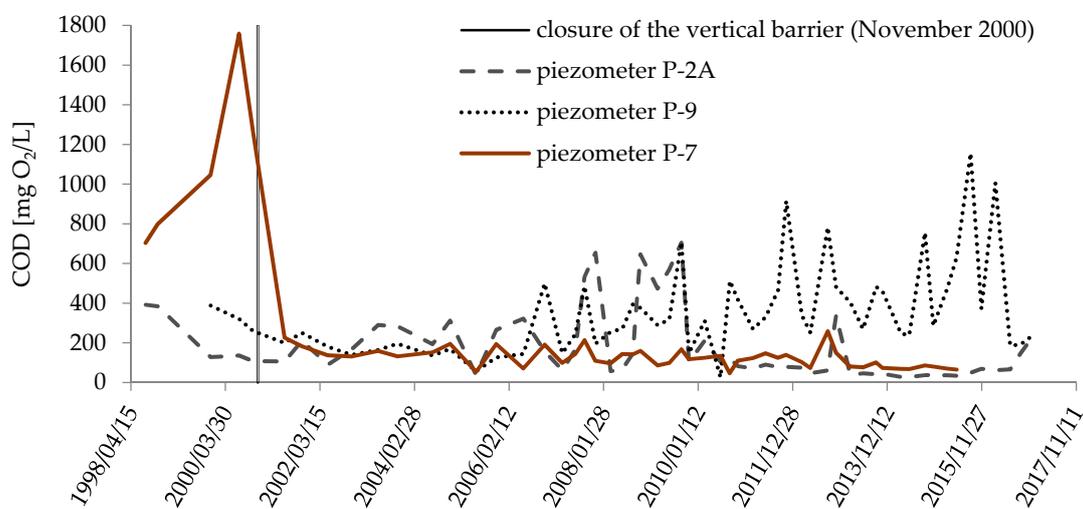


Figure 8. Temporal changes of the COD level in piezometers located in the landfill area.

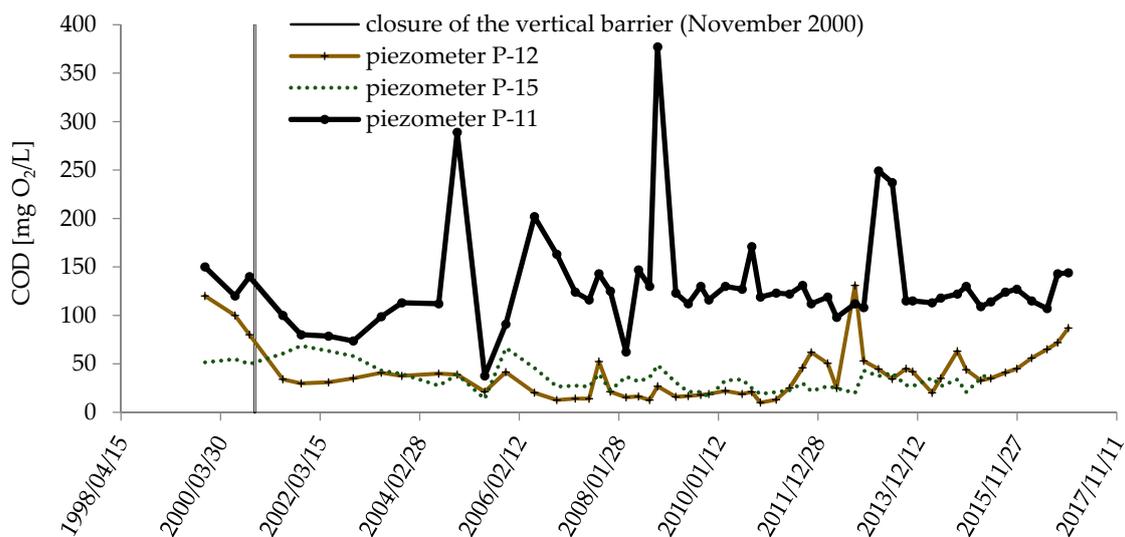


Figure 9. Temporal changes of the COD level in piezometers located in the area of composting plant.

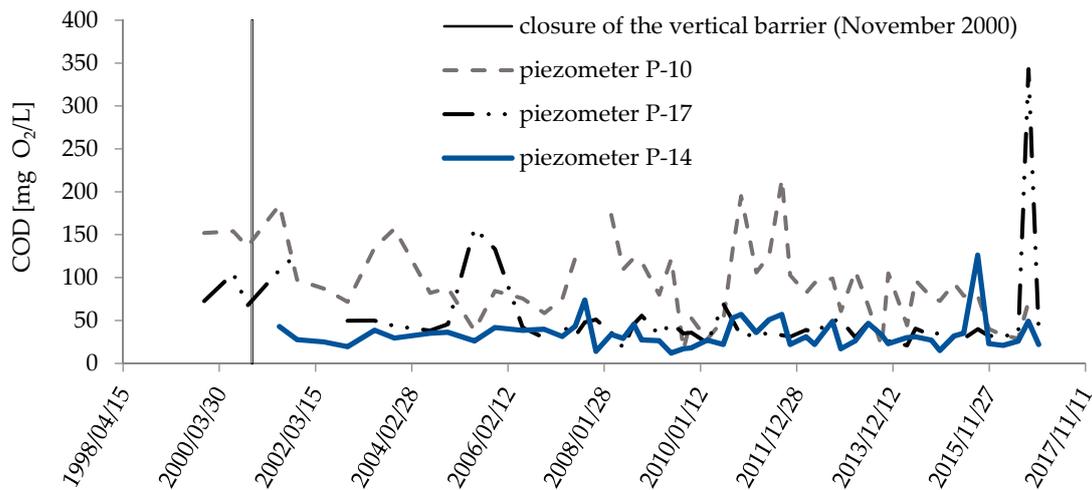


Figure 10. Temporal changes of the COD level in piezometers located in the area of adjacent facilities.

3.2.3. BOD/COD Ratio

The BOD/COD ratio is considered a valuable indicator of organic matter degradation in a landfill [43]. According to Ngang and Agbazue [15], if the BOD: COD ratio in water is found to be higher than or equal to a value of 0.8, the water is said to be highly polluted.

Based on our studies, it can be stated that before the closure of the vertical barrier, the highest values of BOD/COD ratios were observed in piezometer P-9 indicating groundwater pollution in that area. Mean values of BOD/COD ratios detected in the remaining piezometers vary from 0.379 (piezometer P-10A) to 0.539 (piezometer P-4). For comparison, the BOD/COD values obtained in studies conducted at a landfill site located in Finland [44] were in the range of 0.44–0.53. According to Uz et al. [45], these values can be compared to untreated domestic wastewater, for which the BOD/COD ratio varies from 0.4 to 0.8.

After the closure of the vertical barrier (November 2000), all of the mean BOD/COD ratio values became lower than 0.18. Change of the BOD/COD ratios of several orders of magnitude indicates significant improvement of the groundwater quality in the study area. On the other hand, COD indicates the total organic matter content of an effluent, both biodegradable as non-biodegradable, whereas BOD only measures the biodegradable fraction. Thus, the lowest ratio BOD/COD indicates that it has a lower proportion of biodegradability.

Comparison of the minimum, maximum, mean and standard deviation of the BOD/COD ratios obtained for all piezometers during the entire monitoring period are presented in Table 3.

Table 3. BOD/COD ratio for groundwater samples collected in the study area.

Piezometar	BOD/COD Ratio before the Closure of the Vertical Barrier				BOD/COD Ratio after the Closure of the Vertical Barrier			
	Min	Max	Mean	STD	Min	Max	Mean	STD
P-2A	0.370	0.663	0.490	0.132	0.003	0.352	0.119	0.119
P-4	0.279	1.055	0.539	0.448	0.001	0.481	0.105	0.127
P-6A	0.260	0.673	0.493	0.206	0.011	0.469	0.118	0.123
P-7A	0.370	0.498	0.415	0.072	0.007	0.384	0.144	0.121
P-9	0.560	2.062	1.561	0.708	0.005	0.610	0.140	0.155
P-10A	0.368	0.390	0.379	0.016	0.004	0.487	0.139	0.136
P-11A	n.d.	n.d.	n.d.	n.d.	0.004	0.445	0.133	0.139
P-12	n.d.	n.d.	n.d.	n.d.	0.011	0.671	0.146	0.137
P-14A	0.270	0.560	0.454	0.150	0.016	0.543	0.155	0.119
P-17	n.d.	n.d.	n.d.	n.d.	0.012	0.439	0.171	0.132

Note: n.d. (not detected).

3.2.4. Total Organic Carbon (TOC) in Groundwater

TOC (total organic carbon) is considered as the most relevant parameter for quantifying organic pollution in water [46]. The Regulation of the Minister of the Environment of Poland on the criteria and method of evaluating the underground water condition sets the upper acceptable limit for TOC in groundwater at the level of 10 mg C/L. Comparison to the results obtained in our studies (Figures 11–14) indicates that the groundwater is contaminated by organic chemicals. The highest values are observed nearest the landfill (piezometers P-7A (in 2007), P-9 (in 2015) and P-2A (in 2006)). However, Figure 12 shows that level of TOC in piezometer P-7 was stable during analyzed period (from 1998 to 2016) as opposed to a piezometer P-9. In piezometer P-2A, after 2009 monitoring data indicate stabilization. In 2016, the concentrations were lower, but still exceeded the maximum allowable limit. The maximum level of TOC is currently observed around piezometers P-9 and P-11A but in piezometer P-11A after 2009 increase in level of TOC was observed. Worthy of note is a fact that piezometer P-11A is located in a local depression, and consequently, water from the railway siding and the composting area can flow down easily to that point and directly cause groundwater pollution in this piezometer. In case of piezometers located in the area of adjacent facilities, after 2009 decrease of the TOC level was observed. Due to the lack of monitoring data from the period before the closure of the vertical barrier, the overall assessment of the impact of the cut-off wall construction on the TOC in groundwater cannot be made.

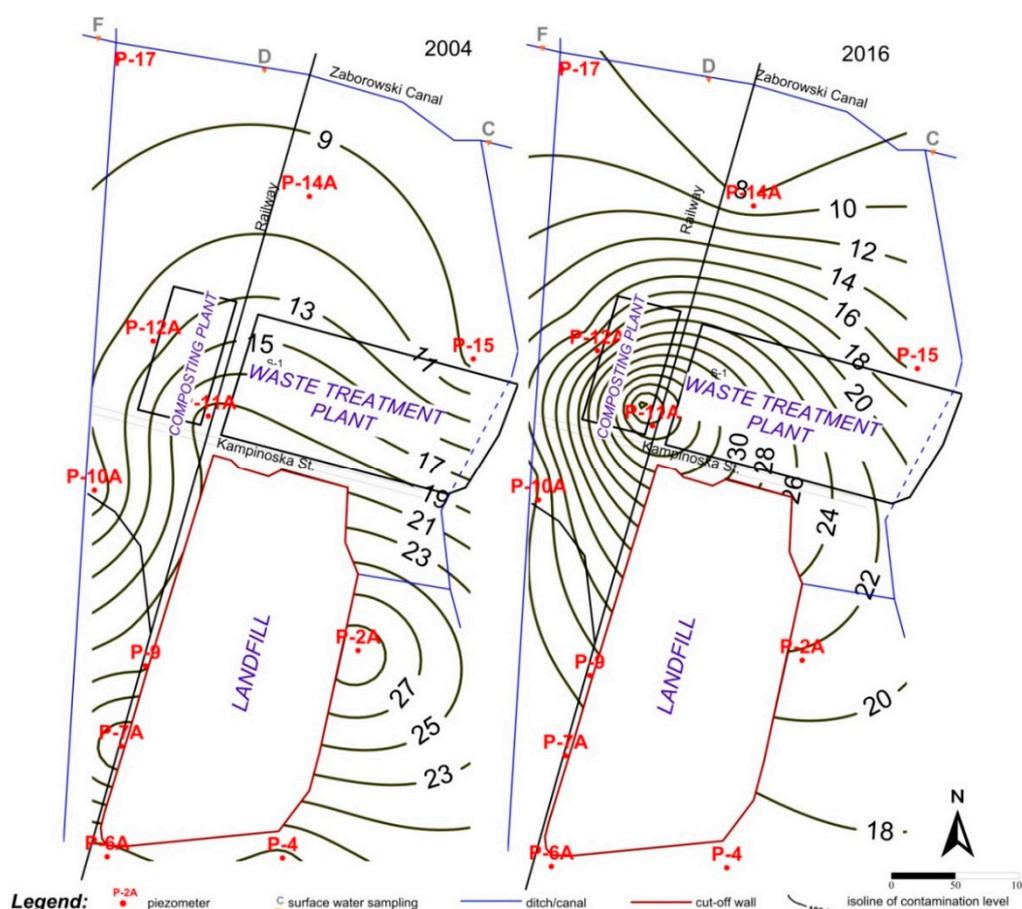


Figure 11. Distribution of the mean values of the total organic carbon (TOC) in groundwater in 2004 and 2016.

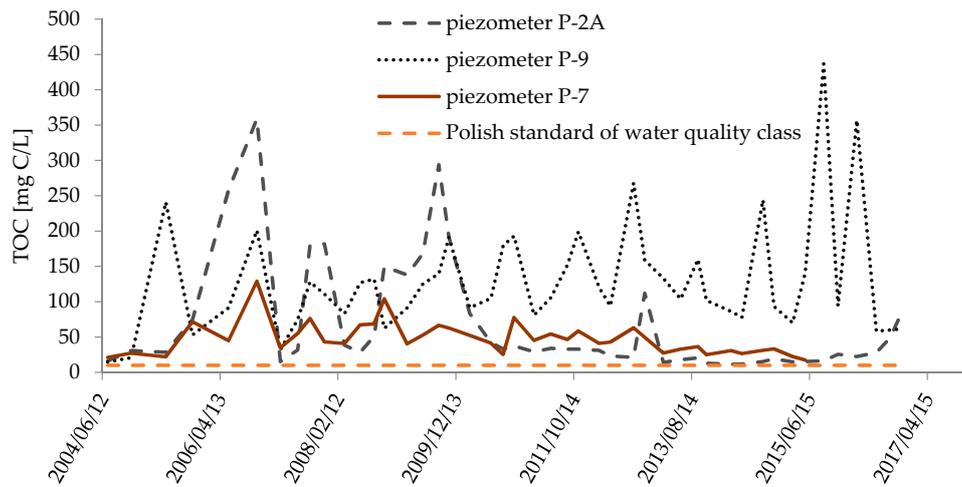


Figure 12. Temporal changes of the TOC level in piezometers located in the landfill area.

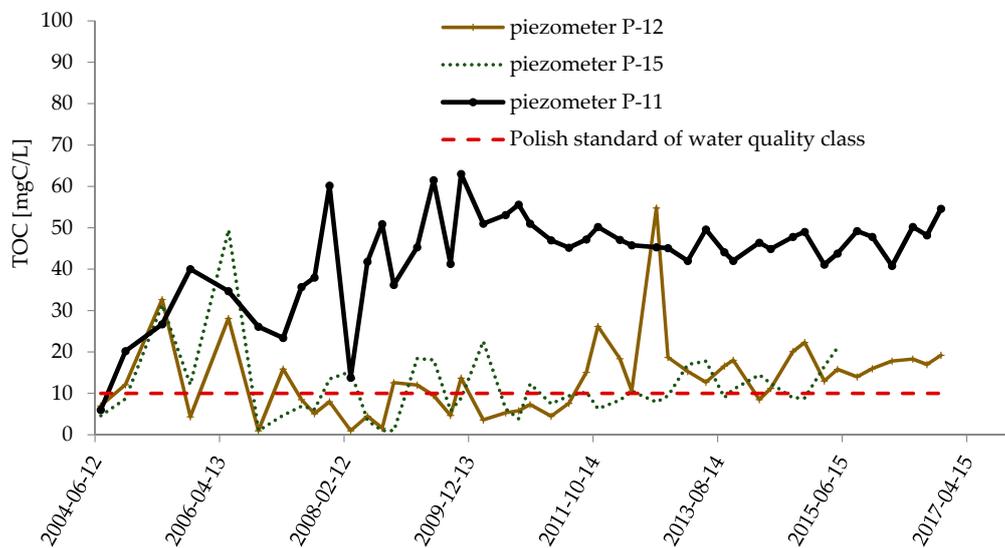


Figure 13. Temporal changes of the TOC level in piezometers located in the area of composting plant.

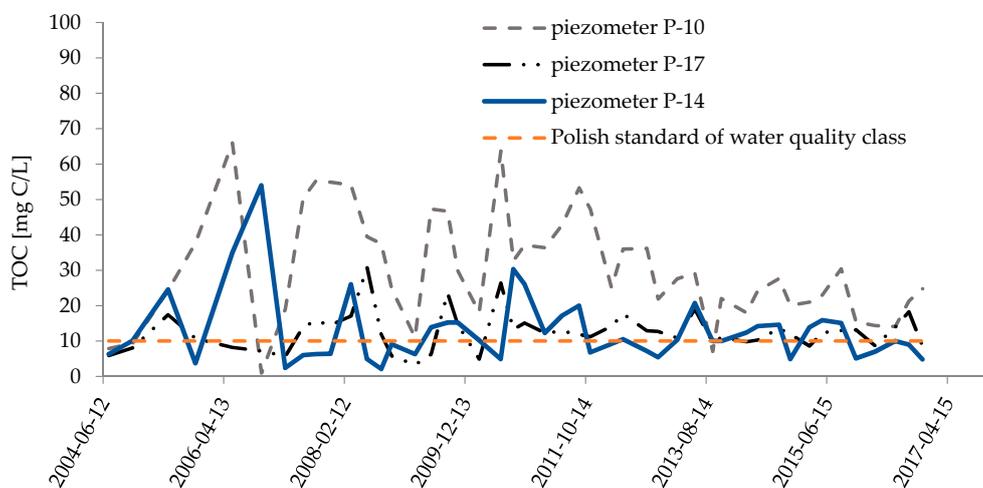


Figure 14. Temporal changes of the TOC level in piezometers located in the area of adjacent facilities.

3.3. Statistical Analysis of the Monitoring Data

3.3.1. Pearson’s Correlation Analysis

Pearson’s correlation analysis between selected pollution indicators were conducted for the monitoring data from piezometers located within the landfill, the composting plant, and the area of the adjacent facilities. Out of a total of 30 correlations (10 for each piezometer) calculated between the selected pollution indicators for piezometers located within the landfill area, 13 were found to be significant at a level of $p < 0.05$ (six for piezometer P-2A, four for piezometer P-7A and three for piezometer P-9).

The most significant correlation ($r > 0.8$) was detected between BOD and COD, and EC and COD for piezometer P-2A ($r = 0.859$ and $r = 0.813$, respectively). According to the classification of the correlation coefficient (r) presented by Evans [47], it can be stated that strong correlation exists between BOD and COD, COD and TOC, and COD and EC for groundwater samples taken from piezometer P-7A ($r = 0.621$, $r = 0.652$, $r = 0.679$, respectively). High values of COD compared to BOD and no correlation between them observed in piezometer P-9 can indicate that the major part of organic compounds is not biodegradable. Strong correlation ($r = 0.772$) was also observed between COD and TOC for piezometer P-9, and very strong correlation was observed in groundwater from this piezometer between COD and EC, and TOC and EC concentrations ($r = 0.815$ and $r = 0.826$, respectively) (Table 4). Positive correlations between BOD versus COD ($r = 0.652$), and TOC versus COD ($r = 0.743$) were also obtained by Maitera et al. [48], indicating that both are products of organic matter oxidation.

Table 4. Pearson’s correlation analysis between selected pollution indicators based on monitoring data from piezometers located within the landfill area.

Variable	BOD	COD	TOC	pH	EC
PIEZOMETER 2A					
BOD	1	0.859 *	0.601 *	−0.246	0.649 *
COD		1	0.696 *	−0.154	0.813 *
TOC			1	−0.338 **	0.645 *
pH				1	−0.214
EC					1
PIEZOMETER 7A					
BOD	1	0.621 *	0.378 **	0.052	0.576 *
COD		1	0.652 *	0.268	0.679 *
TOC			1	0.054	0.354 **
pH				1	0.246
EC					1
PIEZOMETER 9					
BOD	1	0.190	0.018	−0.255	0.137
COD		1	0.772 *	−0.004	0.815 *
TOC			1	0.063	0.826 *
pH				1	−0.057
EC					1

* correlation significant at $p < 0.01$ (two-tailed), ** correlation significant at $p < 0.05$ (two-tailed).

For piezometers located in the area of the composting plant and the Municipal Waste Treatment Installation (P-11A, P-12, and P-15), pollution indicators show weaker mutual correlation (Table 5).

Moderate positive correlation was observed between BOD and COD ($r = 0.599$), and TOC and EC ($r = 0.424$) for piezometer P-11A. Moderate negative correlation was observed in this piezometer between BOD and TOC ($r = −0.517$), and BOD and EC ($r = −0.410$). In piezometer P-12, the strongest correlation was calculated between COD and TOC ($r = 0.717$). Moderate correlation exists between COD and EC ($r = 0.589$), and TOC and EC ($r = 0.413$). Other parameters detected for this piezometer have revealed weak ($r < 0.39$) or very weak ($r < 0.19$) correlation. For piezometer P-15, only the relation between BOD and COD was found to be strong ($r = 0.666$). Moderate negative correlation was

observed in piezometer P-15 between BOD and EC ($r = -0.407$). Weak or very weak correlation was calculated among the rest of the selected parameters.

Table 5. Pearson’s correlation analysis between selected pollution indicators based on monitoring data from piezometers located within the composting area.

Variable	BOD	COD	TOC	pH	EC
PIEZOMETER 11A					
BOD	1	0.599 *	-0.517 *	0.102	-0.410 *
COD		1	-0.080	0.303 **	-0.005
TOC			1	0.022	0.424 *
pH				1	-0.201
EC					1
PIEZOMETER 12					
BOD	1	0.308 **	-0.153	0.188	-0.227
COD		1	0.717 *	-0.060	0.589 *
TOC			1	-0.263	0.413 *
pH				1	-0.305 **
EC					1
PIEZOMETER 15					
BOD	1	0.666 *	0.127	0.072	-0.407 *
COD		1	0.124	0.146	0.141
TOC			1	-0.168	0.282
pH				1	0.017
EC					1

* correlation significant at $p < 0.01$ (two-tailed), ** correlation significant at $p < 0.05$ (two-tailed).

Among 30 correlations calculated for parameters measured in the piezometers located in the area of the facilities adjacent to the landfill (Table 6), only one pair of variables has revealed a very strong relation ($r = 0.878$, measured between BOD and COD in piezometer P-14A). In piezometer P-10A, moderate correlation was observed between BOD and COD ($r = 0.462$), and COD and TOC ($r = 0.468$). Correlations between other selected indicators were found to be weak or very weak for this piezometer. With the exception of the correlation between BOD and EC ($r = 0.494$), a similar tendency was observed for parameters analyzed in piezometer P-17.

Table 6. Pearson’s correlation analysis between selected pollution indicators based on monitoring data from piezometers located in the area of the adjacent facilities.

Variable	BOD	COD	TOC	pH	EC
PIEZOMETER 10A					
BOD	1	0.462 *	0.311 **	-0.089	0.517 *
COD		1	0.468 *	0.298 **	0.321 **
TOC			1	0.140	0.369 **
pH				1	-0.380 **
EC					1
PIEZOMETER 14A					
BOD	1	0.878 *	0.052	-0.265	-0.015
COD		1	0.211	-0.237	0.147
TOC			1	-0.313 **	0.352 **
pH				1	-0.133
EC					1
PIEZOMETER 17					
BOD	1	0.352 **	0.014	0.137	0.494 *
COD		1	0.193	0.006	0.232
TOC			1	-0.078	0.004
pH				1	-0.144
EC					1

* correlation significant at $p < 0.01$ (two-tailed), ** correlation significant at $p < 0.05$ (two-tailed).

3.3.2. Box-and-Whisker Plots

The box-and-whisker plots displayed in Figures 15–17 show the minimum, median and maximum tendency, and the extreme results of monitoring data from 1998 to 2016 collected four times a year, usually in March, June, September and November.

The results show that the minimum BOD levels are in the range of 0.5 mg O₂/L for all piezometers but the maximum concentrations are observed in piezometers P-9, P-7A, P-11A and P-2A (800, 650, 600 and 260 mg O₂/L, respectively). However, these values were obtained from the period before the closure of the vertical barrier.

A similar situation was observed in the case of COD concentrations in groundwater. During the 1998–2016 monitoring period, the maximum COD levels were observed in piezometers P-7A (1758 mg O₂/L), P-9 (1157 mg O₂/L), P-2A (705 mg O₂/L) and P-11A (377 mg O₂/L).

In the case of TOC concentrations in groundwater, the minimum levels were observed in piezometers P-10A, P-12, and P-15 (1 mg C/L), and the maximum levels in piezometers P-9, P-2A, and P-7A (437, 359 and 129 mg C/L, respectively). This confirms that the BOD, COD, and TOC concentrations in groundwater are determined by the location of these piezometers.

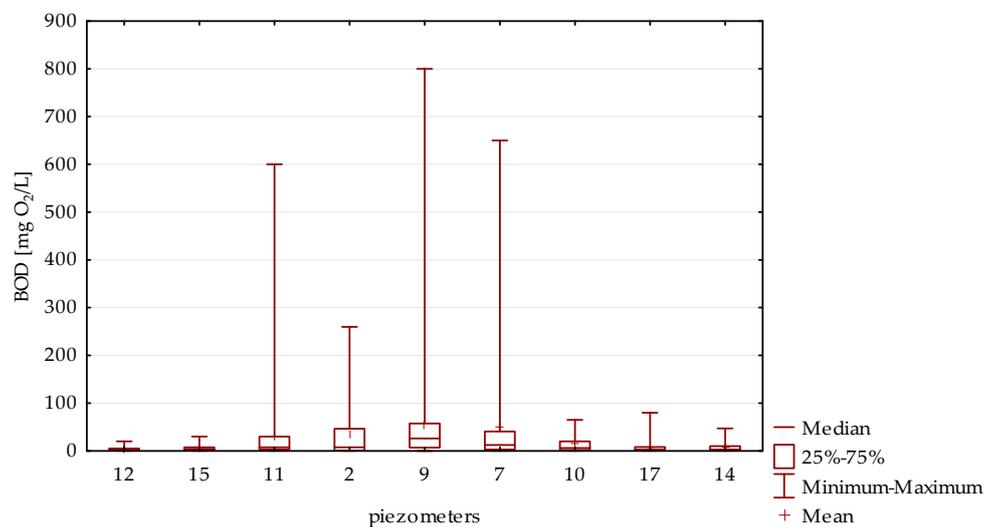


Figure 15. Box-and-whisker plots of the BOD level in particular piezometers.

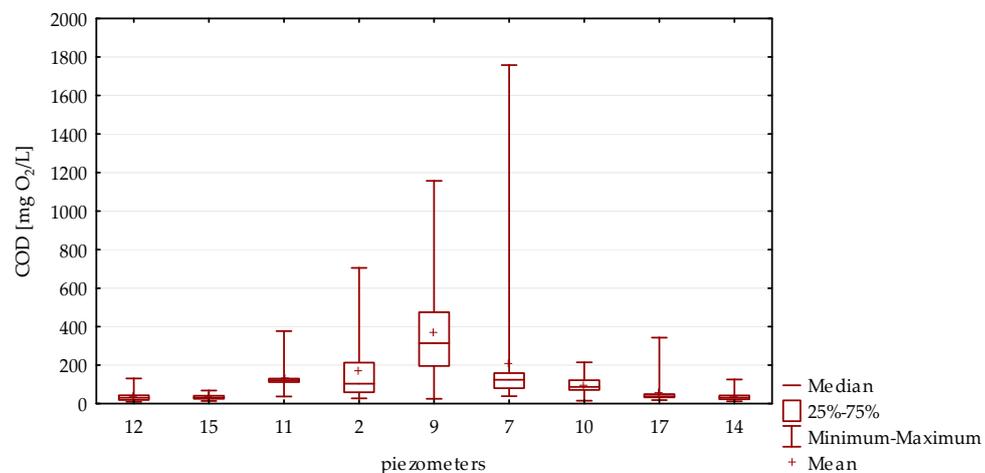


Figure 16. Box-and-whisker plots of the COD level in particular piezometers.

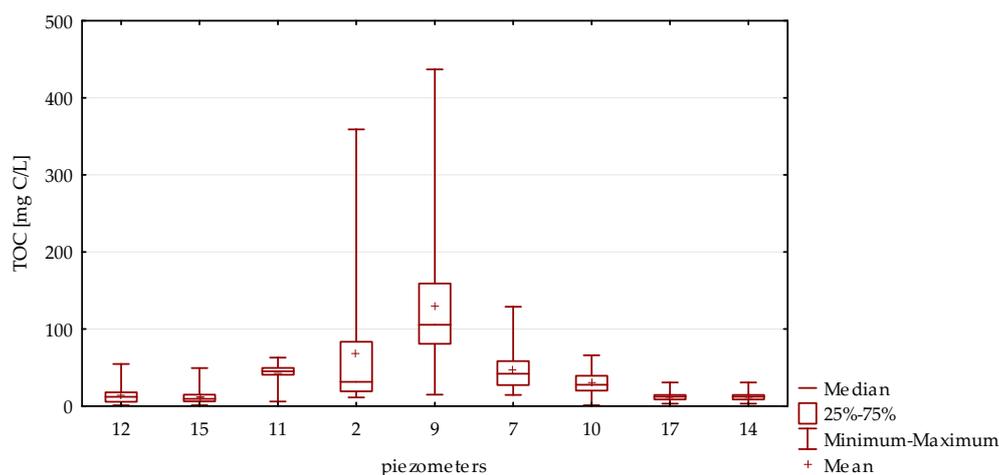


Figure 17. Box-and-whisker plots of the TOC level in particular piezometers.

4. Conclusions

Leachate containing large concentrations of organic compounds can result in many environmental problems, mainly associated with groundwater contamination. This study has shown that trends pointing to the deterioration or improvement of water quality can be determined based on the measurement results coming from longer time spans. Assessment of the results of groundwater monitoring in a landfill site is based on the analysis of pollution indicator parameters. The results of monitoring data presented in this paper clearly indicate the crucial impact of cut-off wall application on the protection of the soil-water environment. The obtained results in some piezometers still exceed standard of the third water quality class established by Polish law. In particular, it is clearly visible for concentration of the total organic carbon which are still observed at the level greater than 10 mg C/L. Comparing the environmental condition from the 1998 to the present state, it can be claimed that a significant improve of groundwater quality is observed.

The obtained results show that the construction of a vertical bentonite barrier has significantly improved water quality in almost all piezometers. For some sampling points, decrease in the value of the parameters was observed by a few orders of magnitude. Especially visible is the decrease of BOD level which is now 160 times lower than in 1998.

Based on the monitoring studies, it can be stated that the most vulnerable to contamination were the areas closest to the landfill and the area of the composting plant. It is also worth noting that external sources can have a great impact on groundwater contamination by organic compounds. As was emphasized in this article, the forest surroundings, putrefaction of vegetal remnants or location of piezometers in the overgrown area can contribute to increased organic pollution indicator levels observed in groundwater samples taken from such location.

Different correlations between parameters obtained for the landfill area and the composting plant may indicate that more factors have a direct impact on pollution indicators in the case of the composting plant. Only a detailed analysis would allow us to find how specific factors influence the correlations that we obtained and certainly we should take into consideration such analysis in our further studies.

Worthy of note is also the fact that seasonal changes of groundwater contamination level can be strictly associated with the groundwater level changes. It was not analyzed in detail for the purpose of this article but based on the monitoring data we can claim that increased values of organic pollution indicator levels correspond to lower groundwater levels. For further studies, it would be valuable to analyze the seasonal pattern of groundwater level changes and resulting in that the variability of measured parameters on an annual basis.

At present, the levels of BOD, COD and TOC in groundwater point to contamination by organic substances in the study area. Thus, the authors point out the need of a re-analysis in the future based on monitoring data covering a longer time span, which should aid in the assessment of the effectiveness of groundwater self-purification.

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Conflicts of Interest: The authors declare no conflict of interest.

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