ASSESSMENT OF GROUNDWATER CONTAMINATION AROUND RECLAIMED MUNICIPAL LANDFILL – OTWOCK AREA, POLAND

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ABSTRACT

The research was conducted around reclaimed landfill, located on the suburb of Otwock, around 25 km south-west of Warsaw. The objective of this study was to identify the chemical composition of groundwater and to determine the landfill impact on the chemical composition of groundwater downgrading from the landfill. Otwock landfill is located in very permeable area, where leachate quickly seeps into groundwater and plays a key role in controlling redox condition (and chemical composition of groundwater) of the downgradient area. High concentrations of HCO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, $Fe_{tot.}$ as well as DOC in groundwater downgradient from the landfill (in comparison to background water) likely indicate that groundwater quality is being significantly affected by leachate percolation. Currently, the load of contamination is released from landfill periodically and slowly moves (70 m/y) in the aquifer along the flow direction. The effect of distance of the piezometer from the pollution source was also investigated. As expected, water from the nearest piezometer to the landfill showed the highest values of contaminant (water temperature, specific electrical conductivity, sodium, iron, chlorides (except for summer and autumn analysis) and calcium (except for winter analysis)). Chemical status of groundwater downgradient from the landfill is poor.

Keywords: landfill, anaerobic conditions, leachate-contaminated water, background water, groundwater quality.

INTRODUCTION

Landfills were constructed without taking too much care of the surrounding environment in early 1960's. Many of them were constructed without appropriate engineering structure to control and minimize the impact of degrading refuse on soil and groundwater quality. Moreover, many of them could contain illegally dumped non-segregated wastes. Landfills were generally not capped after closure to prevent the formation of leachate by infiltration of rainwater, nor were precautions taken to prohibit spreading of leachate to underlying aquifers. Therefore, release of hazardous chemicals to the environment continues, although landfills are closed now. It is commonly known that the quantity of leachate is a function of geological structure (and underlying soil), hydrogeological and climatic conditions as well as the characteristics of the refuse. The quality of groundwater impacted by landfill leachate is highly dependent on the stage of the refuse transformation (the landfill age) and the effectiveness after landfill reclamation. It is commonly observed that despite the reclamation, groundwater quality is being significantly affected by leachate percolation. As a result, leachate plumes have been formed downstream from many landfill sites and have been moved away along the groundwater flow direction.

Similar situation had been suspected around the reclaimed Otwock landfill. The study of hydrogeological conditions and chemical composition of groundwater in the vicinity of this landfill was carried out to asses the impact of the leachate on groundwater quality and to distinguish

natural water-rock interactions and anthropogenic influences.

In the interior of the Otwock landfill, typical anaerobic conditions are observed. It is generally expected that the geochemical condition of landfill will evolve toward an aerobic, but currently measured gases indicated that biochemical processes are still active and landfill gas (biogas) is generated [Porowska, Gruszczyński 2006, 2013]. Very permeable and thin layer of compost receives a large amount of rainwater which infiltrates into the subsurface of the landfill and leachate is generated. Otwock landfill is located in a very permeable area, hence leachate quickly seeps into groundwater and plays a key role in controlling redox condition of the downgradient area, where a distinct contamination was detected. The second factor in the formation of leachate is a shallow position of the water table, reaches as far as the base of the landfill when temporarily part of the landfill body resides below groundwater table. Research indicates that leachate affects on groundwater composition at the downgradient piezometers. This landfill, and other old landfills without liners or leachate collecting systems constitutes a threat to the downgradient groundwater quality due to infiltration of leachate into the aquifer. Leachate plume may be attenuated by natural processes such as dilution, dispersion, diffusion, sorption and biodegradation in the groundwater aquifer system along the groundwater flow direction [Cherry (eds.) 1983, Christensen, Kjeldsen 1989, Christensen et al. 1994]. However, the load of contamination is released from landfill periodically and causes almost continuous (in variable concentrations) contamination downgradient from the landfill. Variations in concentrations of chemical species downgradient of the landfill are controlled by change in leachate composition and mentioned above physical attenuation and chemical reaction [Baedecker, Apgar 1984]. Chemical reactions and processes in contaminated water do not remain constant with time.

The objective of this study was to identify the chemical composition of groundwater and determine landfill impact on chemical composition and quality of groundwater downgradient from the landfill.

This paper presents preliminary results from field and laboratory research of groundwater samples collected from aquifer in Otwock landfill. The physical and chemical constituents discussed here in detail include: water temperature, pH, specific electrical conductivity (SEC), oxidation-reduction potential (ORP), dissolved oxygen (DO), HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $Fe_{tot.}$, as well as dissolved organic carbon (DOC).

MATERIALS AND METHODS

Research site description

Research was conducted around old municipal landfill (after reclamation) located on the suburb of Otwock, around 25 km south-west of Warsaw (Figure 1).

Otwock landfill covers an area of 2,8 ha and received municipal waste in the period 1961–1991 [Koda et al. 1999]. The amount and type of refuse in Otwock landfill is not known (is not well documented), because landfilling was uncontrolled. The landfill has no bottom lined and the waste is placed directly on the ground. After closing, the landfill was covered with a soil layer consisting of approximately 30–50 cm compost and was planted with grass. Landfill leachate is formed from the infiltration and passage of water through solid waste which results in a combination of physical, chemical and microbial processes that transfer pollutants from waste material to the water. The site history and landfill gases composition as well as hydrogeochemical conditions were studied in a previous investigation [Porowska, Gruszczyński 2006, 2013].

The landfill is located on the Vistula river valley, close to the Świder stream. The Świder stream to the north, and Vistula river to the west drain groundwater from the landfill area. According to the groundwater table contour shown on Figure 1, the general flow direction is northwest.

The bedrock of the landfill is represented by river deposit with high permeability – gravels and varigrained sands, locally contain organic matter distribute within aquifer or as a peat layer. The full extent of these peat deposits is not known, but partly include the northern area where piezometer no 2 is located. The hydraulic conductivity of aquifer ranged between 6.5×10^{-4} m/s and 1.6×10^{-3} m/s, depending on the clay content. Groundwater flow velocity, determined by Małecki eds. [2006], is expected to be about 70 m per year. During the periods of high recharge and high river levels (flood peaks in the early spring), the largest part of the landfill body resides below groundwater table, which is less than 2.7 m below ground surface, generally. In the research period, depending
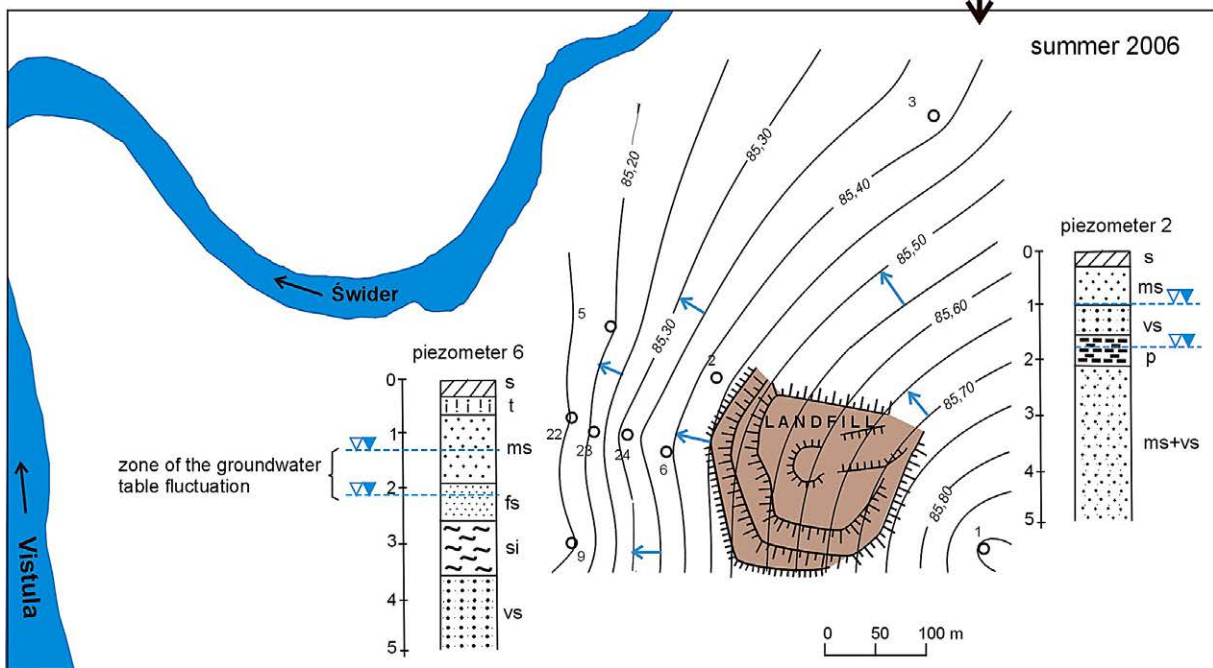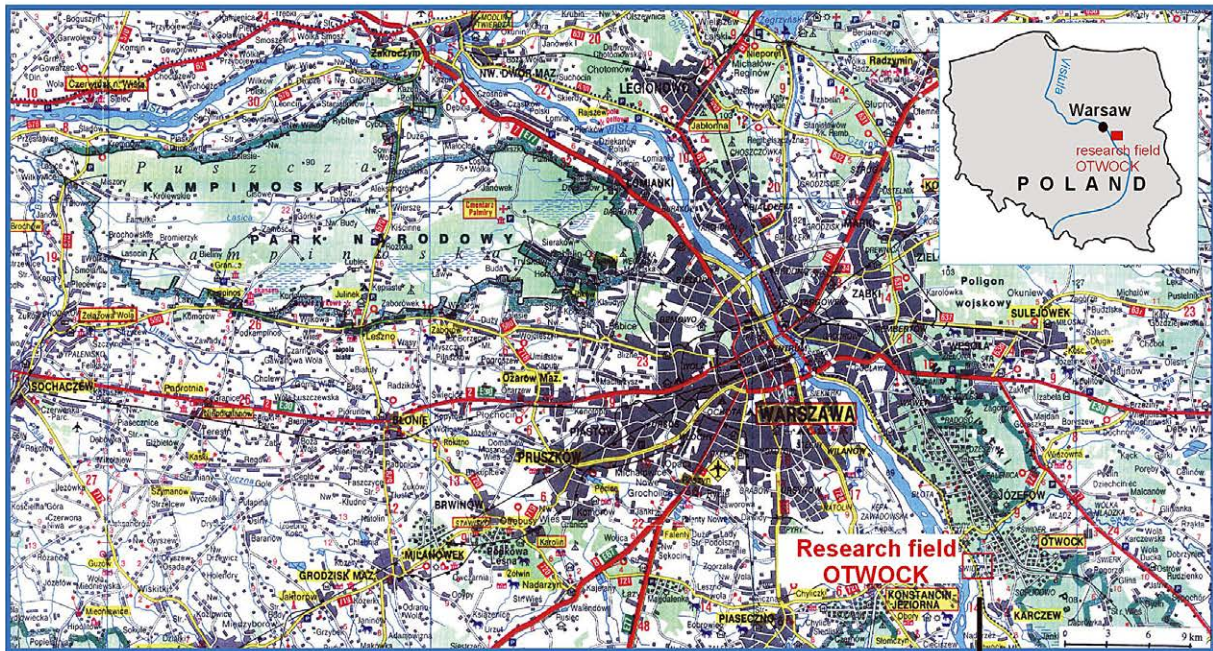
Figure 1. Location and hydrogeological setting of the study area

No piez.	Depth to the groundwater table (m)				Amplitude (m)
	25.05.2006	23.08.2006	8.12.2006	6.03.2007	
22	2,10	2,16	2,31	1,51	**0,80**
6	1,98	2,01	2,16	1,36	**0,80**
23	1,79	1,90	nm	nm	-
24	1,91	2,00	2,17	1,33	**0,84**
2	1,53	1,61	1,77	1,00	**0,77**
1	1,80	2,36	2,66	1,67	**0,99**
3	1,77	1,85	1,96	1,32	**0,64**
5	2,40	2,53	1,81	nm	-
9	1,93	2,04	2,20	nm	-

nm - no measured

on the study site, groundwater table ranged from 1.5 m bgl to 2.7 m bgl (from May to December) and from 1.0 m bgl to 1.7 m bgl (in March) (Figure 1). The annual water level fluctuation is 0.64–0.99 m, but the general groundwater flow direction has not changed.

As it was mentioned above, the water table around the landfill corresponds well to the rainfall and river levels. The thickness of sand between the bottom of the refuse and the water table is relatively thin and additionally is decreased owing to capillary rise (which is greater than 0.3 m in this sediment), thus the aeration zone below the refuse may be thin to non-existent. This short travel distance through the unsaturated zone is unlikely to significantly change the quality of the percolating water. This suggest that spatial differences in chemical compositions of groundwater below the landfill and along the flow direction are due to different chemical processes occurring in the aquifer.

METHODS

To understand a general variation in groundwater chemistry within the study area, the field and laboratory research were conducted quarterly from May 2006 to February 2007 (25.05.2006, 23.08.2006, 8.12.2006 and 6.03.2007). Water samples for chemical analysis were collected within the same aquifer (from similar depth – 3.8 to 4.8 m bgl.) using the PCV piezometers, which were installed in a series along the main direction of groundwater flow as well as above of the landfill (Figure 1). Piezometers localized above of the landfill refereed to background water. Leachate were not analyzed (no water in the ditch on the leachate).

The samples from the piezometers were first taken with an insertion pump with a large pumping capacity, which was pumped long enough to remove the standing water column and/or until constant values were measured for the water temperature, oxidation-reduction potential, content of dissolved oxygen, pH and specific electrical conductivity of the water. Prior to sampling, parameter listed above were measured. A flow-though cell (Eijkelkamp Corp.) was used to improve the comfort and precision of on-line measurements. Water quality characteristics were measured using a portable instruments for analysis in the field: water temperature and pH – pH-meter 330i

(WTW); oxidation-reduction potential (ORP) – pH-meter 330i (WTW) with redox electrode PolyPlast ORP; specific electrical conductivity (SEC) – conductivity-meter CC-401 (Elmetron Corp.); dissolved oxygen (DO) – oxygen meter of the ProfiLine Oxi 197 (WTW). Field measured ORP was corrected to the standard hydrogen electrode [Weight, Sonderegger 2000]. Field sampling was conducted with an emphasis on eliminating potential sources of error associated with water collection and transport to the laboratory. Water samples were collected for laboratory tests according to updated sampling procedures described in: Hermanowicz et al. [1999], Weight and Sonderegger [2000]], Witczak et al. [2013] and Polish Standards. All samples were stored at 4°C until the analysis. Laboratory tests included determination of major ions (HCO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+) and NO_3^-, $Fe_{tot.}$ as well as the content of dissolved organic carbon. The analyses were performed at the Central Chemical Laboratory of Polish Geological Institute - National Research Institute in Warsaw and at the Laboratory of Institute of Hydrogeology and Engineering Geology, Faculty of Geology in Warsaw. Water table contour map were prepared using a computer program Surfer 8.0.

RESULTS AND DISCUSSION

A simple assessment of the impact of the leachate on groundwater quality can be made comparing background water chemistry upstream of the landfill (uncontaminated groundwater) and the worst-case measured chemistry in groundwater below the landfill (leachate-contaminated water) [Basberg et al. 1998]. In order to make such a comparison, research were performed in a series piezometers located along the main groundwater flow direction, downstream of the landfill (inside plume where leachate-contaminated water occurs) and upstream of the landfill (uncontaminated groundwater which can be regarded as background water) (Figure 1). Often the range of the landfill impact on groundwater is difficult to designation due to the lack of clear differences between adjacent samples (e.g. gradual increase in the content of each ions). In this case the division between the two zones (uncontaminated groundwater and leachate-contaminated water) was based on the previously performed analysis of saturation indices (with respect to calcite, do-

lomite and siderite) [Porowska 2010] and based on the relationship between the concentrations of bicarbonates and calcium (Figure 2).

Figure 2 illustrates the relationship between calcium concentrations (mval/dm³) and bicarbonates (mval/dm³) of background water and leachate-contaminated water. This plot clearly indicates which piezometers are influenced by landfill contamination. The samples representing natural conditions are located along 1:1 line and suggest that chemical composition of groundwater (main ions: HCO_3^-, Ca^{2+}) is principally controlled by natural biogeochemical processes (CO_2 generation in the soil and aquifer through the root respiration and the decay of natural organic matter). Groundwater samples collected from contaminated area located below 1:1 line manifest high HCO_3^- concentration in comparison to Ca^{2+} concentration caused by anthropogenic processes (activity of the landfill).
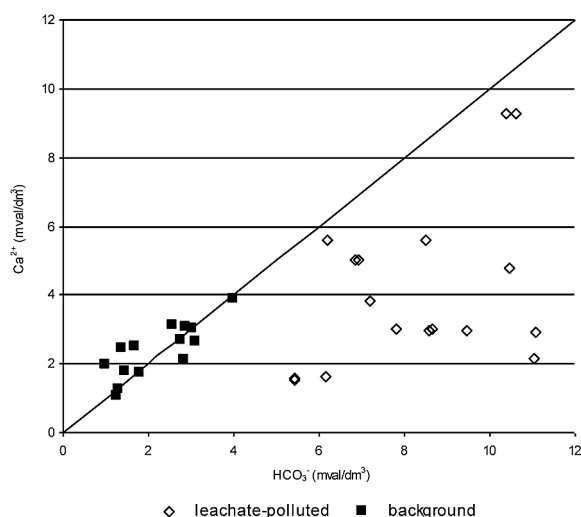

Figure 2. Relationship between calcium and bicarbonates concentrations of groundwater

According to this division, the extreme values of selected parameters and concentrations (as mg/dm³) of major constituents of groundwater around Otwock landfill are shown in Figure 3.

The field measurements of: groundwater temperature, pH, specific electrical conductivity (SEC) and oxidation-reduction potential (ORP) as well as selected ions: HCO_3^-, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and $Fe_{tot.}$ indicates differences between background water and leachate-contaminated water.

Generally, temperatures of the shallow groundwater are dependent on ambient air temperatures, hence the highest values are expected in summer. It is noteworthy that, groundwater temperature was close to landfill body, what depends on not only high ambient air temperatures in summer but much more on the fermentation heat during decomposition of organic wastes (an exothermic reaction). Evidently differences occurred in winter, the minimum temperatures of background water were 1.4 °C while the leachate-contaminated water reached 6.3 °C (Figure 3). The highest groundwater temperatures are observed inside the leachate plume and tend to decrease downstream. Regardless of the research season, the highest water temperature values was measured in the piezometer localized close to the landfill (Figure 4).

The pH of the background water in Otwock was near neutral (slightly acid or slightly alkaline), except winter season, when the pH was higher and its value ranged from 7.30 to 7.68 (Figure 3). This pH values are typical for mature landfills [Tchobanoglous et al. 1993]. The highest pH values was found in groundwater within contaminated zone, regardless of the research season. However, any significant trend of changes in the pH value was not detected with distance from the landfill (Figure 4). A considerable range was found for pH in groundwater (from 7.32 to 7.73) at the landfill border (Figure 3), caused by a number of physical, chemical and microbial processes in the interior of the Otwock landfill.

According to the literature, the major controls on pH in anaerobic leachate are: (1) degradation of organic matter producing large amounts of CO_2, which forms carbonic acid and lowers pH and (2) production of NH_4^+ and CH_4 and reduction of Fe and Mn oxides, all of which consume hydrogen and raise the pH. High pH values within leachate-contaminated water and in background water during winter season indicates the second process is prevailing in Otwock, generally. But the lowest pH values (in comparison to other contaminated water) at the distance between 60 and 90 m from the landfill, indicating influence of organic matter degradation in the interior of the landfill. This situation is possible, because the load of contamination is released from landfill periodically and slowly moves downgradient from the landfill.

Specific electrical conductivity (SEC) is one of the simplest indicators for groundwater contamination by landfill leachate. The SEC of the
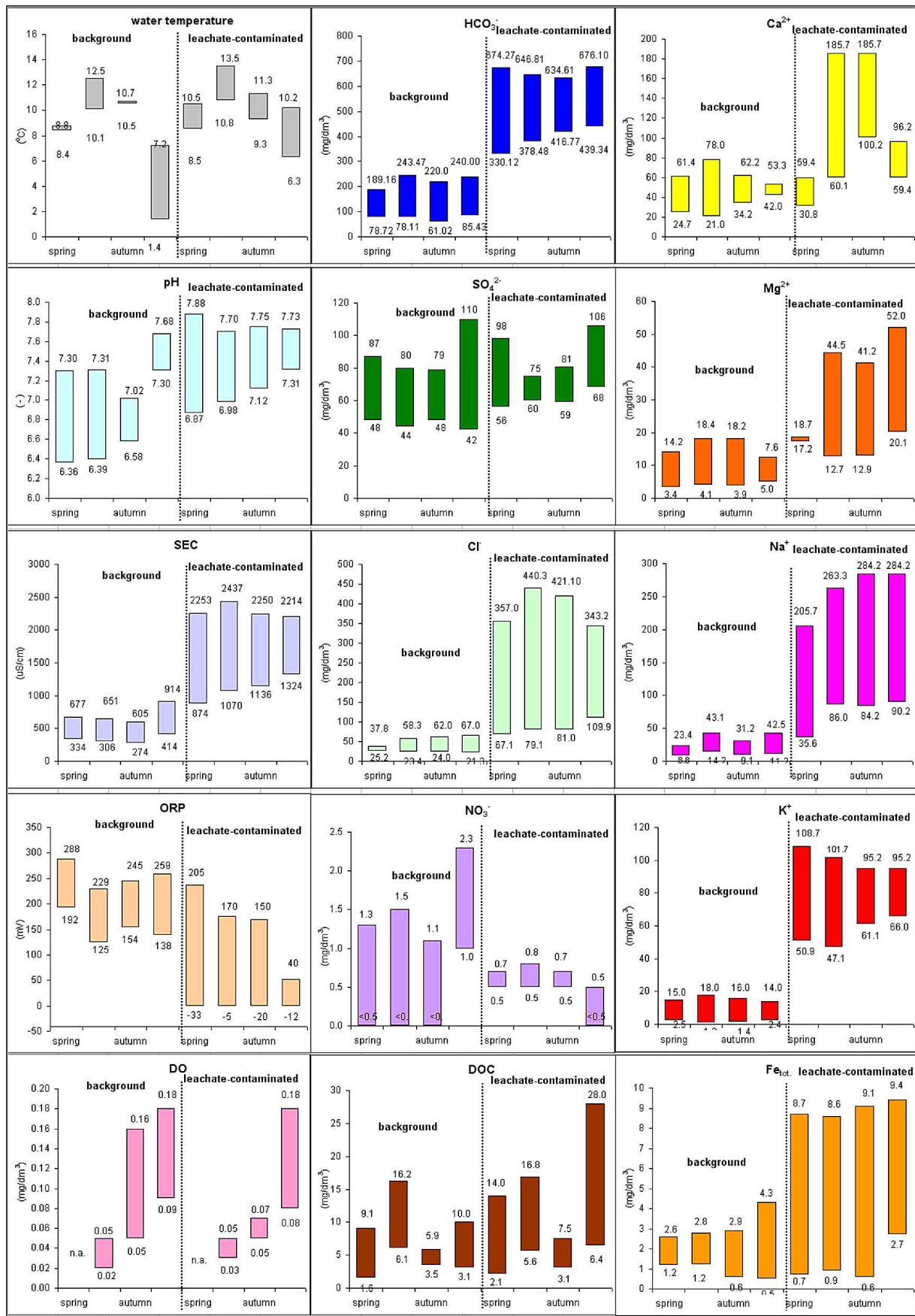
Figure 3. Differences in the values of selected parameters and ions between the background water and leachate-contaminated water
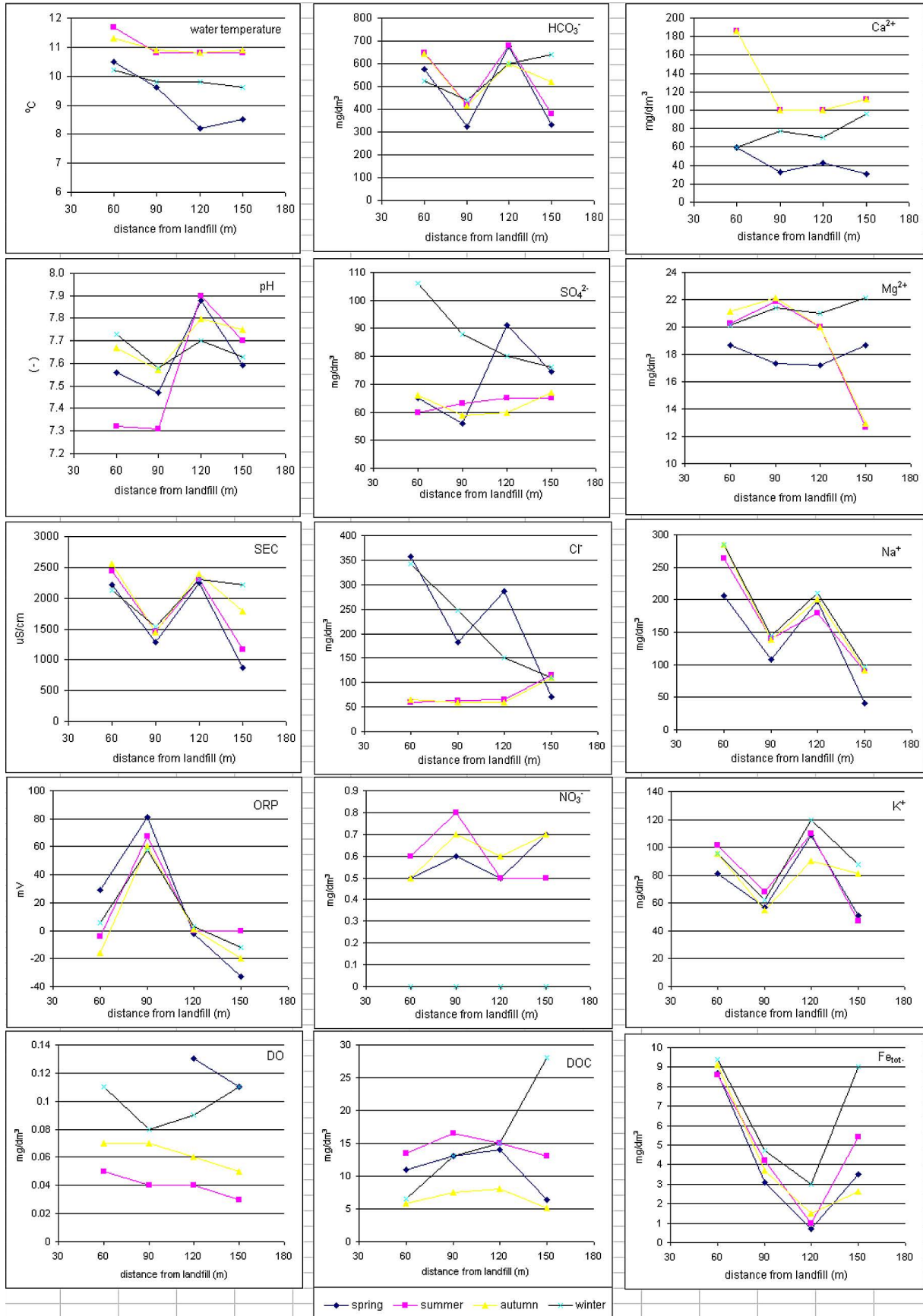
Figure 4. Variations of selected parameters and ions along the groundwater flow direction

background water ranged from 274 to 914 μS/cm and leachate-contaminated – from 874 to 2437 μS/cm (Figure 3). As expected, the groundwater showed very high SEC values within the nearest area of landfill (Figure 4). Similar value was found at the distance between 60 m and 120 m from landfill, indicating two major plumes of leachate moving north-west of the landfill (along the groundwater flow direction). Between two contaminating plumes there is a less contaminated water area. This trend was characteristic for all the measurements, regardless of the research season. Similar trend was observed for the concentration of other ions discussed below (eg. HCO_3^-, Na^+, K^+) (Figure 4). This data indicates that the load of contamination is released from the landfill periodically and slowly moves in the aquifer along the groundwater flow direction. This hypothesis is consistent with other data determined by Małecki eds. [2006] in this area.

Oxidation-reduction potential (ORP) is a useful indicator representing redox condition of groundwater. Redox processes are important in both the production of landfill leachate and the fate of many leachate constituents in the groundwater zone. Redox environments can vary greatly due to contaminant load, groundwater chemistry, geochemistry and microbiology inside the plume and along the flow direction [Christensen at al. 2000a,b, van Breukelen et al. 2003]. A considerable range was found for ORP in groundwater (from -33 mV to 288 mV) in Otwock (Figure 3). The negatives ORP values revealed an anaerobic conditions and were characteristic only for leachate-contaminated water. Outside of the leachate plume, in background water, the minimum ORP values drastically increased up to 125 mV.

ORP does not correspond well to the concentration of the dissolved oxygen (Figure 3), but such a situation is given in the literature [Rose S., Long A. 1988]. Redox potentials cannot adequately predict dissolved oxygen concentrations nor can DO concentrations be used to calculate redox potentials.

Regardless of the research area and season, concentrations of dissolved oxygen are low and not exceed 0,18 mg/dm³ in Otwock. If low oxygen concentration was observed in groundwater above the plume in natural conditions, it can be assumed that there was absent in aquifer before landfilling started. This assumption is very likely in such geological conditions, where organic matter is distributed within the aquifer. According to

this, in Otwock large amounts of DO are removed from the percolation water by the oxidation of organic matter occurred in aquifer (river deposit). After all molecular DO is utilized, organic matter is both oxidized and reduced by anaerobic fermentative processes to produce CO_2 and reduced organic species, such as CH_4. In Otwock methane is produced in the interior of the landfill [Porowska, Gruszczyński 2006] and probably subsequently transported in aquifer and/or partly is oxidized. According to Abichou et. al. [2006] in a landfill intermediate cover, part of methane is oxidized to carbon dioxide (even significantly grater than 25%). This hypothesis needs incontrovertible evidences using carbon isotope analysis in Otwock landfill.

As it was mentioned above, groundwater quality is being significantly affected by leachate percolation downgradient from the landfill. The variation occurs due to spatial and temporal changes in the migration of contaminants from landfill leachate indicated by different values of selected parameters and ions in the same piezometer but in other research period.

Relatively high bicarbonates and chlorides concentrations in groundwater proved that they are all taken from an aquifer zone strongly contaminated by landfill leachate (Figure 3). Bicarbonates concentrations in the plume ranged from 330.12 mg/dm³ to 676.10 mg/dm³, whereas within background water HCO_3^- did not exceed 244 mg/dm³ (Figure 3). Initially, bicarbonates in the plume decreases along the groundwater flow direction from about 600 mg/dm³ at the landfill border to about 400 mg/dm³ at further downstream. At the distance of 120 m HCO_3^- values sharply increased and exceeded even 680 mg/dm³ to subsequently decrease to 300–500 mg/dm³ (except for winter season). High HCO_3^- values at the landfill border are likely to be derived from the biodegradation of organic matter in the interior of the landfill. Organic matter in municipal solid waste landfills typically undergoes methanogenic decomposition, producing carbon dioxide and methane as end products, according to reaction (1) [Hayes 2001]:

$$6CH_2O \rightarrow 3CO_2 + 3CH_4 \qquad (1)$$
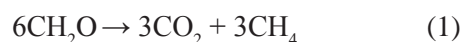
Oxidation of methane in migrating landfill gas to carbon dioxide can occur if the gas travels through a zone with appropriate conditions (access of oxygen or other potential oxidants, such as nitrates or sulfates). This CO_2 combines with water forming carbonic acid, according to reaction (2) [Fetter 1994]:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (2)$$

Carbonic acid dissociates into H^+ and HCO_3^- and may be represented as reaction (3) (depending on pH) [Fetter 1994]:

$$H_2CO_3 \rightarrow HCO_3^- + H^+ \qquad (3)$$
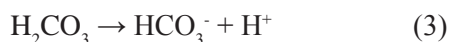
High HCO_3^- concentrations at the distance 120 m from the landfill can be explained that the load of contamination is release from landfill periodically and slowly moves downgradient from the landfill, depending on the climatic and hydrogeological conditions (precipitation, river levels and groundwater table fluctuations).

Sulfates concentrations were independent on the sampling site and similar values (ranged from 42 to 110 mg/dm³) were found in both the leachate-contaminated groundwater and natural water (Figure 3). Regardless of the sampling area it is observed that the sulfates distribution differs from that of other ions and is different in each sampling season (Figure 4). This variability is dependent on climatic and hydrogeological conditions (precipitation and groundwater table elevation). Relatively high sulfates content in this environment indicates a weak reduction of the ion into a form of lower oxidation state (eg sulfides), both inside plume and in natural conditions.

Based on the comparison of hydrogen sulfide in the biogas and sulfates in groundwater [Porowska in press] was found that the sulfates content in the analyzed groundwater, not only due to the activity of the landfill but also of hydrogeochemical processes occurring in the aquifer.

Chlorides are considered a conservative parameter and they are not sensitive to oxidation-reduction reaction. An excess of chlorides concentrations in water is usually taken as an index of pollution and considered as a tracer of groundwater contamination [Macioszczyk, Jeż 1995]. Chlorides can also be used as an ideal indicator of the position of an overall leachate plume. According to this, such concentrations of chlorides confirm the above-mentioned principle that pollution loads are released from the landfill at a certain time (pulse) and their concentrations, are variable in time and in different places. (Figure 4). The highest Cl⁻ concentrations in groundwater occurred close to the landfill (350 mg/dm³), and decreased to about 100 mg/dm³ at 150 m downgradient from the landfill. This suggests a significant dilution of leachate in the aquifer. Such a significant reduction of Cl⁻ concentration in a short distance, allows the assumption that other processes

(e.g. dispersion, diffusion) are of negligible importance in comparison to dilution process. This trend was found in winter while in other seasons it was different (Figure 4). In summer and in autumn Cl⁻ value only slightly exceeded 50 mg/dm³ at the distance of 60–120 m at the landfill border. It is noteworthy that, regardless of sampling season and different values along the groundwater flow direction, at the distance of 150 m from the landfill, chlorides fluctuate around 100 mg/dm³. It can be seen, the hydrogeochemistry changed little in time for the last piezometer. Chlorides values 100–400 mg/dm³ are typical for mature landfills [Tchobanoglous at al. 1993].

Nitrates concentration only was above 2 mg/dm³ within the aquifer upstream of the landfill (natural conditions). Usually, higher nitrates concentrations was observed in background water in comparison to the leachate plume. The presence of elevates levels of nitrates in background water is considered to be due to the excess oxidation-reduction potential values (more oxygenated conditions). Nitrates reduction probably causes disappearance of nitrates downstream of the landfill. Processes causing this decrease are discussed below (reaction 5). A single measurement of the concentration of NH_4^+ showed higher values in the contaminated zone (0.74–5.4 mg/dm³) compared with background water (0.16–0.92 mg/dm³). Similar trend was observed by Cozarelli et al. [2011] in groundwater at the Norman landfill. Hence, it can be assumed that the dominant species of nitrogen in this contaminated environment is an ammonium ion.
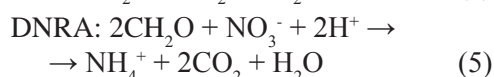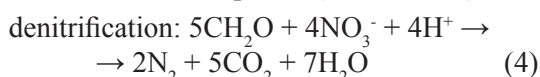
Leachate-contaminated water contain high concentrations of the following ions: Ca^{2+}, Mg^{2+}, Na^+, K^+ and Fe_{tot} in comparison to background water (Figure 2). They show variable concentrations in the plume, but no identical tendency along the groundwater flow direction (except Na^+ and K^+) (Figure 4). Sodium and potassium concentrations are change along groundwater flow direction similar to SEC and bicarbonates, indicating the highest values at the landfill border and at the distance 120 m from the landfill. These parameters confirm the mentioned above principle, that the load of contamination is release from landfill periodically and slowly moves downgradient from the landfill.

Calcium concentrations are low in the plume in comparison to sodium and potassium concentrations. In natural conditions calcium concentrations prevail sodium and potassium con-

centrations. It can be assumed that low calcium concentrations is caused by precipitation carbonate minerals ($CaCO_3$) in leachate-contaminated aquifer [Porowska 2010]. It is commonly known that supersaturation for $CaCO_3$ as well as other carbonates is observed at other landfill leachate plumes [eg. Van Breukelen 2003, Manning 2001].

Chemical analysis of the groundwater indicated a slight difference in the concentrations of the dissolved organic carbon (DOC) between the leachate-contaminated water and background water (Figure 3). Similar values are likely to be derived from the biodegradation of organic matter in the interior of the landfill as well as organic matter, which occur within aquifer sediments. DOC concentrations differs more with time and at the distance, especially 150 m from the landfill (Figure 4). In this place, DOC concentrations increase from 5 mg/dm^3 in autumn to the highest value of 28 mg/dm^3 in winter. Low DOC concentrations suggest biodegradation within aquifer sediments [Christensen at al. 1998].

Biodegradation of organic matter is a very important process in this aquifer, because it plays a key role in shaping hydrogeochemical processes of the selected ion concentrations in groundwater, such as nitrates or sulfates. Thermodynamically, the oxidation of dissolved organic carbon (DOC) is coupled with the reduction of DO, NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, and CO_2, which is predicted to occur in that order [Champ et al. *1979*]. In general, as the DOC is oxidized, DO is preferentially consumed. After the depletion of DO, the next available electron acceptor will be consumed following the sequence described above (aerobic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, sulfates reduction, and methanogenesis). Accordingly, the process of denitrification [e.g. Pedersen et al. 1991] and/or dissimilatory nitrates reduction to ammonium (DNRA) [eg. Tiedje et al. 1982] are possible by slight reduction of the conditions in the plume (reaction 4, 5).

$$\text{denitrification: } 5CH_2O + 4NO_3^- + 4H^+ \rightarrow$$
$$\rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (4)$$

$$\text{DNRA: } 2CH_2O + NO_3^- + 2H^+ \rightarrow$$
$$\rightarrow NH_4^+ + 2CO_2 + H_2O \qquad (5)$$

As it was mentioned above, nitrates concentrations were lower in the leachate plume in comparison to background water in Otwock landfill (Figure 3), caused by nitrates reduction, according to the above reaction: denitrification (4) and/or dissimilatory nitrates reduction to ammonium (5).

The importance of denitrification, as a major pathway of nitrates removal from aquifers, has been reported in many studies. Primary redox processes involve the oxidation of organic carbon and release of reduced redox species (CH_4, H_2S, Fe(II), Mn(II)). These reductants become oxidized in secondary redox processes. At the fringe of a leachate plume in particular, secondary redox processes happen and compete with organic carbon degradation processes for available electron-acceptors [Van Breukelen 2003].

On the base of the research in Otwock it can be assumed that CO_2 released (according to reaction 4 and 5), is dissolved (reaction 2) and dissociates (reaction 3). In the pH range near neutral, dissolution of CO_2 generates bicarbonates ion, which prevail other species of CO_2. It also needs to be considered that high HCO_3^- concentrations in the plume downstream from the landfill can be caused by biodegradation of organic contaminants proceed from the interior of the landfill (reaction 1).

One of the several methods for assessing groundwater quality is to compare the physical and chemical parameters with the limits for groundwater listed in Polish Standards [Journal of Laws No. 143, item 896] (Table 1).

According to this classification of good quality water belongs to classes I–III, and the poor quality water – to classes IV–V. Comparison of groundwater quality along the groundwater flow direction with the highest admissible values in class I–V shows that the: pH, water temperature, NO_3^-, Mg, SO_4^{2-}, Ca lie within the normative range to the class I–III, whereas the content of other parameters: DOC, SEC, DO, Cl^-, K^+, Na^+, HCO_3^-, Fe_{tot} is exceeded and water belong to the classes IV–V (Table 1). Summarizing, chemical status of groundwater along the flow direction is poor.

CONCLUSIONS

Field and laboratory researches of groundwater around Otwock landfill were performed in order to identify the chemical composition of groundwater and assess the landfill impact on the quality of groundwater downgradient from the landfill. The following conclusions can be drawn from the physical and chemical data derived from this study:
1. Despite the storage of waste was finished in 1991, the site has been reclaimed, groundwater quality is being significantly affected by leachate percolation downgradient from the

Table 1. Assessment of groundwater quality along the groundwater flow direction according to Polish Standards [Journal of Laws No. 143, item 896]

Parameter	Unit	Limit values in class I–V					Distance from the landfill [m]			
		I	II	III	IV	V	60 (n=4)	90 (n=4)	120 (n=4)	150 (n=4)
pH	–	6.5–9.5			<6.5 lub >9.5		7.32–7.73	7.31–7.58	7.70–7.78	7.59–7.75
Dissolved organic carbon (DOC)	mgC/l	5	10	10	20	>20	5.8–13.5	7.5–16.5	8.0–15.0	5.1–28.0
Specific electrical conductivity (SEC)	uS/cm	700	2500	2500	3000	>3000	2121–2550	1288–1536	2253–2400	879–2214
Temperature	°C	<10	12	16	25	>25	10.2–11.7	9.6–10.9	8.2–10.8	8.5–10.9
Dissolved oxygen (DO)	mg/l	>1	0.5–1	<0.5	<0.5	<0.5	0.05–0.11	0.04–0.08	0.04–0.13	0.03–0.13
NO_3^-	$mgNO_3/l$	10	25	50	100	>100	0–0.6	0–0.8	0–0.6	0–0.7
Cl^-	mgCl/l	60	150	250	500	>500	60.0–356.98	59.0–247.57	60.0–286.42	70.01–114.50
Mg^{2+}	mgMg/l	30	50	100	150	>150	18.65–21.10	17.30–22.10	17.20–21.00	12.65–22.10
K^+	mgK/l	10	10	15	20	>20	81.35–101.70	55.10–68.15	90.00–120.00	47.05–87.50
SO_4^{2-}	$mgSO_4/l$	60	250	250	500	>500	60–106	56–88	60–91.2	65–76
Na^+	mg Na/l	60	200	200	300	>300	205.7–284.2	108.6–144.6	180.0–210.0	40.75–96.5
Ca^{2+}	mgCa/l	50	200	200	300	>300	59.4–185.7	32.3–100.2	42.8–100.0	30.8–111.6
HCO_3^-	$mgHCO_3/l$	200	350	500	800	>800	523.55–646.81	325.27–439.54	600.00–680.00	330.12–638.27
Fe_{tot}	mgFe/l	0.2	1	5	10	>10	8.6–9.4	3.1–4.7	0.72–3.0	2.6–9.0

landfill. Hydrogeological and climatic conditions play a key role in groundwater chemistry in landfill and surrounding area. Most of the water reaches to the landfill and subsequently to the aquifer by precipitation. A highly permeable, sandy aquifer provides favorable conditions for the transport of contamination into the aquifer. In addition during periods of high groundwater table large part of the landfill body resides below groundwater table. In this situations the load of contamination is release from landfill and moves in the aquifer along the flow direction.

2. Chemical composition of groundwater and hydrogeochemical processes downgradient from the landfill do not remain constant with time. Plume of leachate migrates from the landfill along the groundwater flow direction (70 m/y). In comparison to landfills reported in the literature, the contaminated zone is restricted to relatively small area, owing to location close to Vistula and Świder rivers.

3. Contaminations of groundwater below the landfill have been identified by comparing the chemistry of the water above and below the landfill and by comparing the chemistry of water with quality standards for ground-

water [Dz. U. Nr 143, poz. 896]. The values of: groundwater temperature, pH, specific electrical conductivity (SEC) and oxidation-reduction potential (ORP) and concentrations of selected ions: HCO_3^-, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and Fe_{tot} indicates differences between background water and leachate-contaminated water and evidence of groundwater contamination. As expected, the nearest piezometer from the landfill showed the highest values of water temperature, specific electrical conductivity, sodium, iron, chlorides (except for summer and autumn analysis) and calcium (except for winter analysis). A comparison of groundwater quality along the groundwater flow direction with the highest admissible values [Journal of Laws No. 143, item 896] shows that the chemical status of groundwater along the flow direction is poor.

4. The load of contamination and concentration in groundwater depends on the following factors: 1) dilution of leachate with uncontaminated groundwater, 2) mixing of anaerobic leachate with oxygenated water that facilitates the decomposition of organic matter and precipitation of metals, and 3) interaction of contaminants with aquifer materials and organic matter.

5. The result of these investigations indicated that leachate contaminate the environment, even after the reclamation of landfill. For this reason, the site developed for future landfilling should have a planned engineering structure to control and minimize the impact of landfill leachate on groundwater quality around the landfill.

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