Landfill leachate quantity and attenuation distance of inorganic contaminants in the groundwater of different hydrogeological systems: a case study of Lithuania

Gintarė Slavinskienė, Arūnas Jurevičius, Jonas Satkūnas, Rasa Šimanauskienė

Abstract. This study examines the relationship between the quantity of landfill leachate and attenuation distance of inorganic contaminants in the groundwater of open, semi-open and closed hydrogeological systems. Nearly 2,000 groundwater samples were collected and 12 inorganic chemical parameters were investigated, of which NH_4^+, K^+ and Fe were considered to be the most groundwater polluting chemical parameters. Analytical modelling of pollution migration, multivariate statistical techniques and a single factor pollution index method were applied for data processing. The results showed that irrespective of waste volume, the degradation coefficients of NH_4^+, K^+ and Fe were by 36–90% higher in the groundwater of open hydrogeological systems, where attenuation distances were by 14–56% shorter compared with those in closed hydrogeological systems. Also, the degradation coefficients of NH_4^+, K^+ and Fe^+ in the groundwater of very small and small landfills were by 37–90% higher and attenuation distances were by 38–99% shorter compared with those in the groundwater of large and very large landfills. In the groundwater of very small and small landfills the difference between NH_4^+, Fe and K^+ attenuation distance in open and closed hydrogeological systems was about 89–97% lower than the difference in large and very large landfills. This finding indicates that the quantity of leachate is the main factor of attenuation of contaminants in groundwater. The results obtained in this research may be used to predict the dispersion of pollution in the groundwater of landfills located in similar hydrogeological systems and to take environmental protection measures.

Keywords: *landfill; leachate quantity; inorganic contaminants; attenuation distance; hydrogeological systems*

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INTRODUCTION

There are a number of closed or abandoned landfills in the world, installed without any technical means to prevent or limit landfill leachate migration into groundwater. The pollution of groundwater by these landfill contaminants causes significant damage to the natural environment and can affect human health. Many studies have revealed that the main categories of contaminants from landfills include organic matter, inorganic salts, heavy metals, bacteriological contaminants and xenobiotic organic compounds (Christensen *et al.* 2001; Han *et al.* 2016; Lee *et al.* 2007). The review study by Han *et al.* (2016) identified 96 kinds of contaminants in groundwater in the proximity of landfills. Concentrations of 22 kinds of contaminants significantly exceeded drinking water quality standards and were considered very dangerous. Other studies reported that most of obvious groundwater pollution generally occurred after approximately 5 to 25 years (Bakis, Tuncan 2011; Han *et al.* 2016; Navarro, Carbonell 2008). These facts indicate that research of groundwater pollution by landfill leachate is very important and relevant in

particular for the countries where the main source of potable water is groundwater (Kadūnas *et al.* 2017).

The horizontal distribution of leachate plume mostly depends on the lithology of aquifers, age of the landfill, quantity and quality of leachate, and hydrodynamic and hydrochemical processes occurring in the landfill leachate-polluted groundwater along the flow path. The volume of waste and the hazard level of landfill contaminants determine the quantity and quality of leachate entering the groundwater. Many studies were performed in order to estimate the horizontal distance of the leachate plume (Basberg *et al.* 1998; Christensen *et al.* 2001; Fernandez *et al.* 2014; Han *et al.* 2016; Liedl *et al.* 2005; Longe, Enekwechi 2007; Maier, Grathwohl 2006; Xie *et al.* 2016).

However, the studies listed above are examples of the assessment of point sources of pollution in groundwater of local hydrogeological conditions or review studies of the total plume length. These studies lack the assessment of the horizontal distribution of the leachate plume, depending on hydrogeological conditions, the quantity and quality of leachate, and kinds of chemical parameters on the regional scale. The present study, therefore, aims to 1) identify the degree of inorganic parameters pollution in

the groundwater of the most polluted hydrochemical zones; 2) determine the attenuation distances of inorganic parameters, which account for the highest degree of pollution, in groundwater along the flow path; 3) determine the landfill waste volume; 4) discuss the impact of hydrochemical and hydrodynamic processes on the relationship between the quantity of landfill leachate and attenuation distance of inorganic parameters, which account for the highest degree of pollution on the regional scale.

MATERIALS AND METHODS

Description of the study area

A total of 142 closed unlined municipal landfills located across the territory of Lithuania were selected for this study (Fig. 1). The landfills received waste in the period 1985–2012. In this period the mean annual temperature in Lithuania was approximately 6.0–6.5°C, the annual mean precipitation was approximately 600–650 mm, and evaporation was approximately 520–540 mm. In general, most of the precipitation (60–66%) in Lithuania falls in the warm season (April–October).

The mean thickness of Lithuania's Quaternary deposits is 130 m and varies from 10–30 m in the
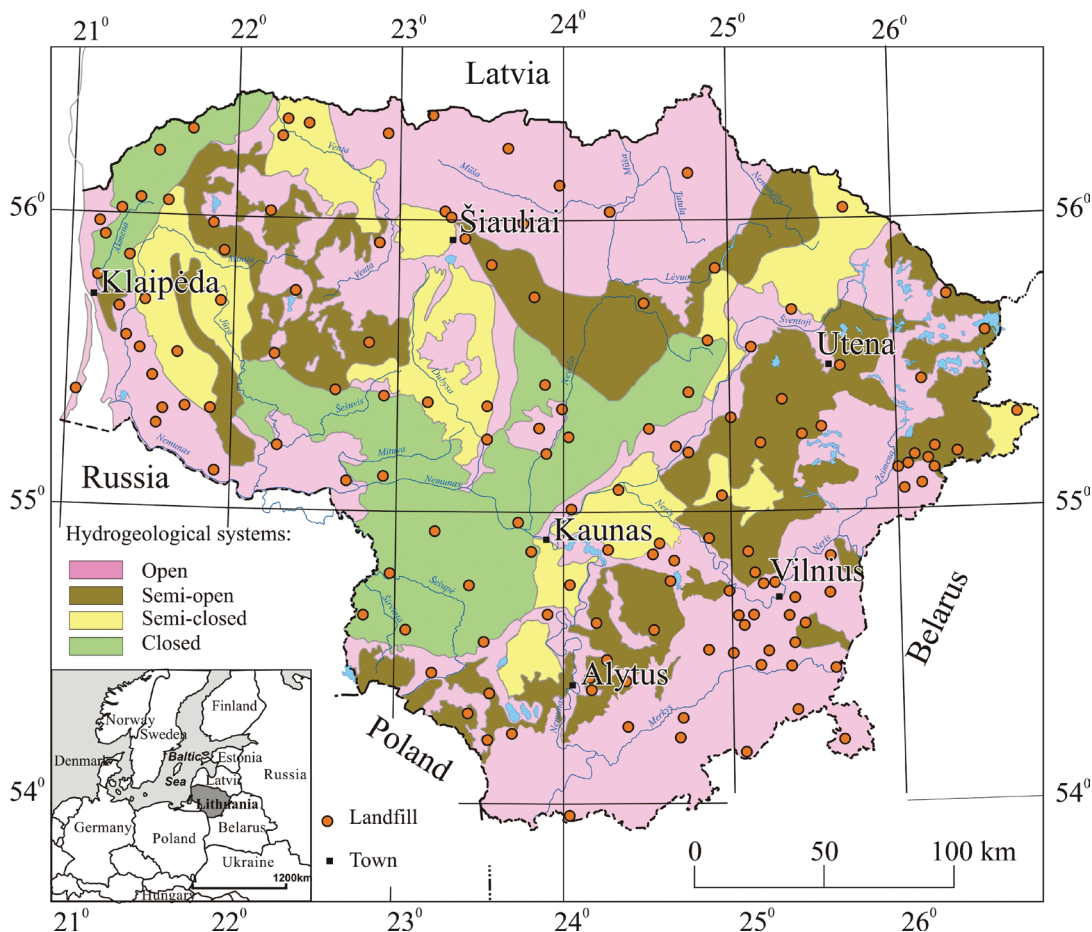

Fig. 1 Map of the location of the study landfill sites

northern part of the country, that is, the area of prevailing glacial erosion, up to 200–300 m in the marginal and insular glacial Uplands and buried valleys or palaeoincisions (Guobytė, Satkūnas 2011). Sandy and clayey deposits of glacial origin prevail in the Quaternary cover. Pre-Quatenary sandy, clayey and carbonate rocks and sediments are located below the Quaternary, and the depth of the active groundwater exchange zone is 200–300 m (Grigelis *et al.* 1994). The investigations of the present study focused on the groundwater aquifer situated in the upper part of the sedimentary cover (up to 50 meters deep) which is particularly vulnerable to surface pollution. Groundwater was found in the sand and gravel of fluvial, glaciofluvial and glaciolacustrine intercalated with clayey layers. The vulnerability of the active water exchange zone to anthropogenic pollution across the territory of Lithuania is influenced by different geological and hydrogeological characteristics such as natural isolation and filtration properties in the upper part of the sedimentary section. The vulnerability characteristic depends on the ratio between sandy and clayey layers. Based on these characteristics, the territory of Lithuania is divided into four categories (Baltrūnas *et al.* 1998): areas of very high vulnerability (open hydrogeological systems), areas of high vulnerability (semi-open hydrogeological systems), areas of medium vulnerability (semi-closed hydrogeological systems) and areas of low vulnerability (closed hydrogeological systems) (Table 1, Fig. 2). The lithology of prevailing sediments in hydrogeological systems determines their inherent filtration properties: with the increasing amount of clay particles the potential of pollution filtration decreases, i.e. pollutant filtration becomes slower and more complex.

In the present study, semi-closed and closed hydrogeological systems were treated as one system. The deposits of semi-closed and closed hydrogeological systems have similar hydraulic conductivity parameters; therefore, hydrochemical and hydrodynamic processes have similar effects on attenuation of chemical parameters. As a result, semi-closed and closed hydrogeological systems were treated as one closed hydrogeological system.

Data collection and analysis

The groundwater samples used in this research were collected from landfill sites in 1997–2015. A total of 2,200 samples were taken from 582 observation wells during this period. The depth of observation wells was approximately 25 m. The wells installed in landfills had a diameter of 50–100 mm. Well screens contained gravel filters whose thickness was > 20 mm. Well casings and screens were made from chemically resistant polyvinyl chloride (PVC). Wellheads were protected from accidental pollution by impact-resistant covers. While taking groundwater samples, the wells were cleaned using special bailers: in this way, 3 volumes of groundwater that the well could contain were pumped out. The bailer was washed with clean water before immersion in the next well. Samples were collected in 500 ml plastic bottles prepared in the laboratory and within 24 hours were transported in a freezer to the laboratory.

The chemical composition of these groundwater samples were analysed in the laboratories licensed by the Lithuanian Environmental Protection Agency using methodologies approved by the Lithuanian Standards Board. Major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}) were measured by ion chromatography. HCO_3^- was measured by potentiometric titration, permanga-
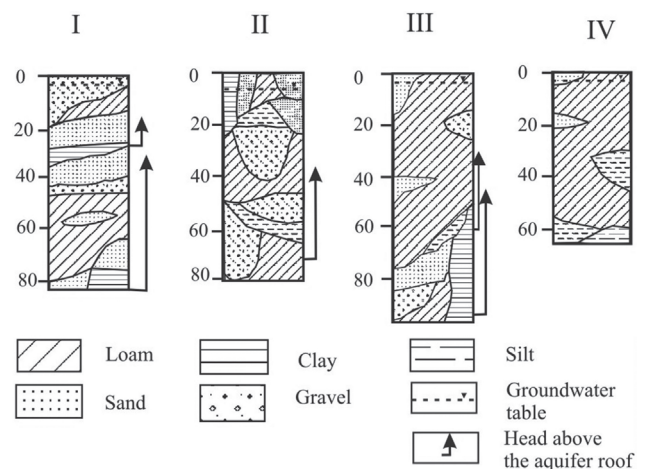

Fig. 2 Types of hydrogeological systems: I – open, II – semi-open, III – semi-closed, IV – closed. Hydrogeological profiles by Baltrūnas *et al.* (1998)

Table 1 Types of hydrogeological systems and their characteristics

No.	Hydrogeological systems	Vulnerability of the area	Lithological characteristics	Hydraulic conductivity, m/d	Modules of infiltration recharge, L/s·km²
I	Open	Very high	Homogeneous sandy and gravel aquifers prevail, loose water-permeable rock.	1–100	4–6
II	Semi-open	High	Heterogeneous layers, ratio of clay layers makes more than 40–50% of sedimentary section.	> 0.005	2–3
III	Semi-closed	Medium	Heterogeneous layers, ratio of clay layers makes more than 60% of sedimentary section.	0.001–0.005	1–2
IV	Closed	Low	Homogeneous layers of low permeability, ratio of clay layers makes more than 90% of sedimentary section.	≤0.0001	<1

nate oxidation COD_{Mn} by titrimetric, and biogenic components (NO_2^-, NO_3^-, NH_4^+,) were determined using a spectrophotometric method and ion chromatography. Fe was measured spectrophotometrically and by atomic absorption spectrometry. Total dissolved solids (TDS) were determined by calculating the total amount of anions and cations dissolved in the groundwater. The reliability of groundwater samples was assessed by calculating ion-balance errors where the errors were generally within 5%.

Identification of the degree of inorganic parameter specific pollution

The single factor pollution index method was used to assess groundwater quality from the most polluted groundwater zones according to each chemical parameter. The single factor pollution index can be determined using the following expression (Huang *et al.* 2018):

$$P_i = \frac{C_i}{S_i} \qquad (1)$$

where P_i is the pollution index for the ith chemical parameter; C_i is concentration for ith chemical parameter, mg/L; and S_i is the background value for ith chemical parameter, mg/L. The degree of groundwater pollution is classified into five categories according to the single factor pollution index of ith chemical parameter: $P_i \leq 1$ no pollution, $1 < P_i \leq 5$ light pollution, $5 < P_i \leq 10$ moderate pollution, $10 < P_i \leq 50$ heavy pollution, and $P_i > 50$ severe pollution (Huang *et al.* 2018).

Determination of attenuation distances of inorganic parameters

The exponential decrease of chemical parameters in groundwater along the flow path due to degradation can be expressed by Eqs. (2–3) (Huang *et al.* 2017):

$$C_t = C_0 \cdot e^{-\alpha X}, \qquad (2)$$

$$X = \frac{\ln C_0 - \ln C_t}{\alpha}, \qquad (3)$$

where C_0 is the concentration of chemical parameter in groundwater from the most polluted hydrochemical zone (initial), mg/L. This zone coincides with or is in closest proximity to landfill areas, and concentrations of its chemical parameters are very close to those of the leachate. α is the degradation coefficient of a chemical parameter, d^{-1}. C_0 and α are assessments from the exponential diagram. C_t is the background concentration of a chemical parameter in groundwater (mg/L), and X is the distance from the point source of contamination (m) where the concentration of the chemical parameter in groundwater does not exceed the background concentration. This distance in the present study is defined as the attenuation distance of a chemical parameter.

Determination of the landfill waste volume and quantity of inorganic parameters

The calculations of the landfill waste volume were conducted according to the truncated pyramid volume (Eq. (4)), the components of which were obtained by assessing the dimensional parameters of the landfill environment (natural terrain or quarry). The dimensions were assessed using the services of the Lithuanian spatial information portal (Lithuanian spatial information portal 2018).

$$V_{avg} = \frac{1}{3} H_{avg} \left(A_{base} + A_{top} + \sqrt{A_{base} \cdot A_{top}} \right), \qquad (4)$$

where V_{avg} is the mean volume of the landfill (m^3), A_{base} represents the landfill base area (m^2), A_{top} is the top of the area (m^2), and H_{avg} represents the mean height of the landfill (m) (Sokolovas 2005). The quantity of inorganic parameters can be determined using the following expression:

$$W = V \cdot C_0 / 10^6, \qquad (5)$$

where W is the quantity of chemical parameter, t; V is the waste volume of landfill, m^3; and C_0 is the concentration of chemical parameter in groundwater from the most polluted hydrochemical zone (initial), mg/L.

Hierarchical cluster analysis

The hierarchical cluster analysis (algorithm) was used to classify the waste volume and degradation coefficient of Cl$^-$. The analysis was performed using Microsoft Excel @-add-in module XLSTAT. The hierarchical cluster analysis is a mathematical statistics method that determines similarities between objects and divides them into clusters (Vasanthavigar *et al.* 2013). The Euclidean metric was used to assess similarities between objects. Ward's method was used to assess similarity between clusters.

RESULTS

Degree of inorganic parameter specific pollution in groundwater from the most polluted hydrochemical zones

The single factor pollution index (P_i) values for all inorganic parameters in the groundwater of the study landfill sites are shown in Table 2. The pollution index of NH_4^+ with a mean value of 383 was the highest among all components. This value shows a very high degree of ammonium pollution. Similarly, a very high degree of pollution was recorded for K^+ and Fe with the mean pollution index values of 71 and 57, respectively. A high degree of pollution was recorded for NO_2^-, Na^+, Cl$^-$ and COD_{Mn} with the mean pollution index values of 48, 25, 21 and 18, respectively. The mean pollution index values of SO_4^{2-}, NO_3^-, TDS and HCO_3^- ranged from 5 to 10 and indicated a moderate

Table 2 Descriptive statistics of the single factor pollution index (P_i) in the groundwater of the study landfill sites

Parameter	Unit	BV f III/ g III	Minimum	Maximum	1st quartile	Median	3rd quartile	Mean	Standard deviation
NH_4^+	mg/L	0.14/0.88	0.04	7,179	1.79	11.17	125.47	383.01	1,098
K^+	mg/L	1.6/4.1	0.28	2,025	2.22	10.20	38.19	70.93	239.73
Fe	mg/L	0.23/1.0	0.05	522.93	2.96	14.09	62.97	56.58	102.30
NO_2^-	mg/L	0.03/0.03	0.33	2,841	0.33	1.67	11.52	48.05	253.17
Na^+	mg/L	7/17.4	0.23	410.31	1.71	5.70	25.42	24.63	51.80
Cl^-	mg/L	14.8/23	0.08	389.01	1.31	4.44	19.84	21.34	45.07
COD_{Mn}	mg/L O_2	2.58/3.05	0.19	480.12	1.65	5.01	12.54	18.49	48.01
SO_4^{2-}	mg/L	24.8/31.5	0.06	478.51	1.53	3.11	8.38	9.53	40.75
NO_3^-	mg/L	2.69/2.77	0.02	94.56	0.28	2.43	7.55	8.73	17.17
TDS	mg/L	378/563	1.00	58.80	2.46	4.00	7.03	6.91	8.37
HCO_3^-	mg/L	210/375	0.06	76.98	1.77	2.91	4.96	5.21	9.43
Ca^{2+}	mg/L	60.9/69	0.13	25.45	1.87	2.88	4.21	3.61	3.25
Mg^{2+}	mg/L	19.6/34.8	0.09	52.11	0.97	1.83	3.46	3.17	5.24

BV Natural background concentration values of chemical components in the groundwater in sandy (f III) and clayey (g III) deposits (Diliūnas *et al.* 2004).

degree of pollution. A light pollution of groundwater with Mg^{2+} and Ca^{2+} was with the mean P_i values of these components ranging from 3 to 5. The results indicate that P_i of NH_4^+, Fe and K^+ was the highest compared with other inorganic parameters analysed. Therefore, it may be concluded that these chemical parameters were major contaminants of groundwater in the study landfills located in different hydrogeological systems.

Attenuation distance of the major inorganic contaminants

The mean attenuation distance for Fe was the longest compared with attenuation distances for NH_4^+ and K^+ in the groundwater of the analysed hydrogeological systems. The mean attenuation distance and the mean degradation coefficient for Fe in groundwater in different hydrogeological systems ranged from 287 m to 659 m and from 0.004 to 0.04 d^{-1}, respectively (Table 3). Meanwhile, the mean attenuation distance and the mean degradation coefficient for K^+ were in the intervals of 122–142 m and 0.02–0.08 d^{-1}, respectively. The shortest attenuation distances in groundwater were typical of NH_4^+. The mean attenuation distance and the mean degradation coefficient for NH_4^+ were in the intervals of 75–93 m and 0.04–0.06 d^{-1}, respectively (Table 3). Cl^- is a non-reactive chemical parameter; therefore, its degradation in groundwater is controlled only by dispersion and dilution processes (Van Breukelen *et al.* 2004). In order to determine the effect of hydrodynamic processes on attenuation distances in groundwater, the Cl^- chemical parameter was also analysed in greater detail. The mean attenuation distance and degradation coefficient for Cl^- were in the intervals of 81–119 m and 0.02–0.07 d^{-1}, respectively. According to Christensen *et al.* (2001) and Han *et al.* (2016), groundwater pollution mainly appeared within

Table 3 Statistical summary of attenuation distances and degradation coefficients for major inorganic contaminants in the groundwater of the study landfill sites

Para- meter	Open hydrogeo- logical system		Semi-open hydrogeological system		Closed hyd- rogeological system	
	X, m	$α$, d^{-1}	X, m	$α$, d^{-1}	X, m	$α$, d^{-1}
NH_4^+	75.47	0.061	76.20	0.058	92.78	0.039
K^+	121.73	0.082	141.82	0.042	122.67	0.017
Fe	287.22	0.039	364.61	0.009	659.18	0.004
Cl^-	119.33	0.067	96.33	0.049	81.46	0.023

$α$ degradation coefficient of a chemical parameter, X attenuation distance of a chemical parameter.
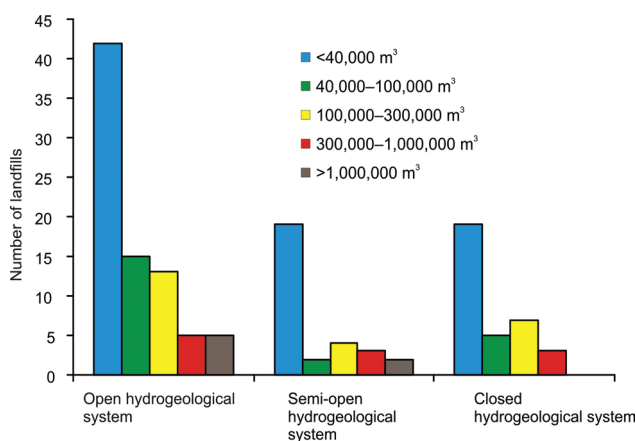
Fig. 3 Distribution of landfills by volume

1,000 m of a landfill. As can be seen from the results obtained, attenuation distances of the analysed chemical components did not exceed the said 1,000 m limit.

Waste volume of landfills

Following the hierarchical clustering of the waste volume, five groups were identified: very small landfills (<40,000 m³), small landfills (40,000–100,000 m³), medium landfills (100,000–300,000 m³), large land-

fills (300,000–1,000,000 m³) and very large landfills (>1,000,000 m³) (Fig. 2). The volume of waste in open hydrogeological systems ranged from 1,000 m³ to 4,500,000 m³ (Fig. 3). Very small landfills dominated (28%). Large (3%) and very large (3%) landfills accounted for the smallest share. The volume of waste in semi-open and closed hydrogeological systems ranged within 1,600–2,000,000 m³ and 4,000–760,000 m³, respectively (Fig. 3). Very small landfills dominated (6–13%) in these systems. Only a small amount of landfills (1–2%) were large or very large.

DISCUSSION

Impact of hydrochemical and hydrodynamic processes on the relationship between the quantity of landfill leachate and attenuation distance of major inorganic contaminants

The relationship between the attenuation distance of NH_4^+, Fe and K^+ in groundwater and the waste volume of landfills can be characterised by the following general trends: 1) irrespective of waste volume, the attenuation distances in the groundwater of open hydrogeological systems were shorter compared with those in semi-open and closed hydrogeological sys-

tems; 2) with the increase of waste volume, the attenuation distances in groundwater in all hydrogeological systems were proportionally longer; 3) with the increase of waste volume, the difference between attenuation distances in open hydrogeological systems and that in closed hydrogeological systems increased proportionally.

The attenuation distance of NH_4^+ in the groundwater of open hydrogeological systems was on average 19% shorter (Fig. 4A) and the mean degradation coefficient was about 36% higher than those in closed hydrogeological systems (Fig. 4B).

The above trend is associated with differences in the intensity of nitrification and dilution process responsible for controlling NH_4^+ degradation. It is known that in groundwater in sandy deposits a continuous supply of oxygen along the flow path is taking place (Wang *et al.* 2015). Furthermore, sandy deposits are conducive to the growth of the nitrifying bacteria population (Buss *et al.* 2004; Zuo *et al.* 2017). As a result, intense microbiological ammonium oxidation is taking place in groundwater in sandy deposits (Eq. (6)). Meanwhile in clayey deposits, due to low oxygen exchange, nitrification in groundwater is very slow (Christensen *et al.* 2001):
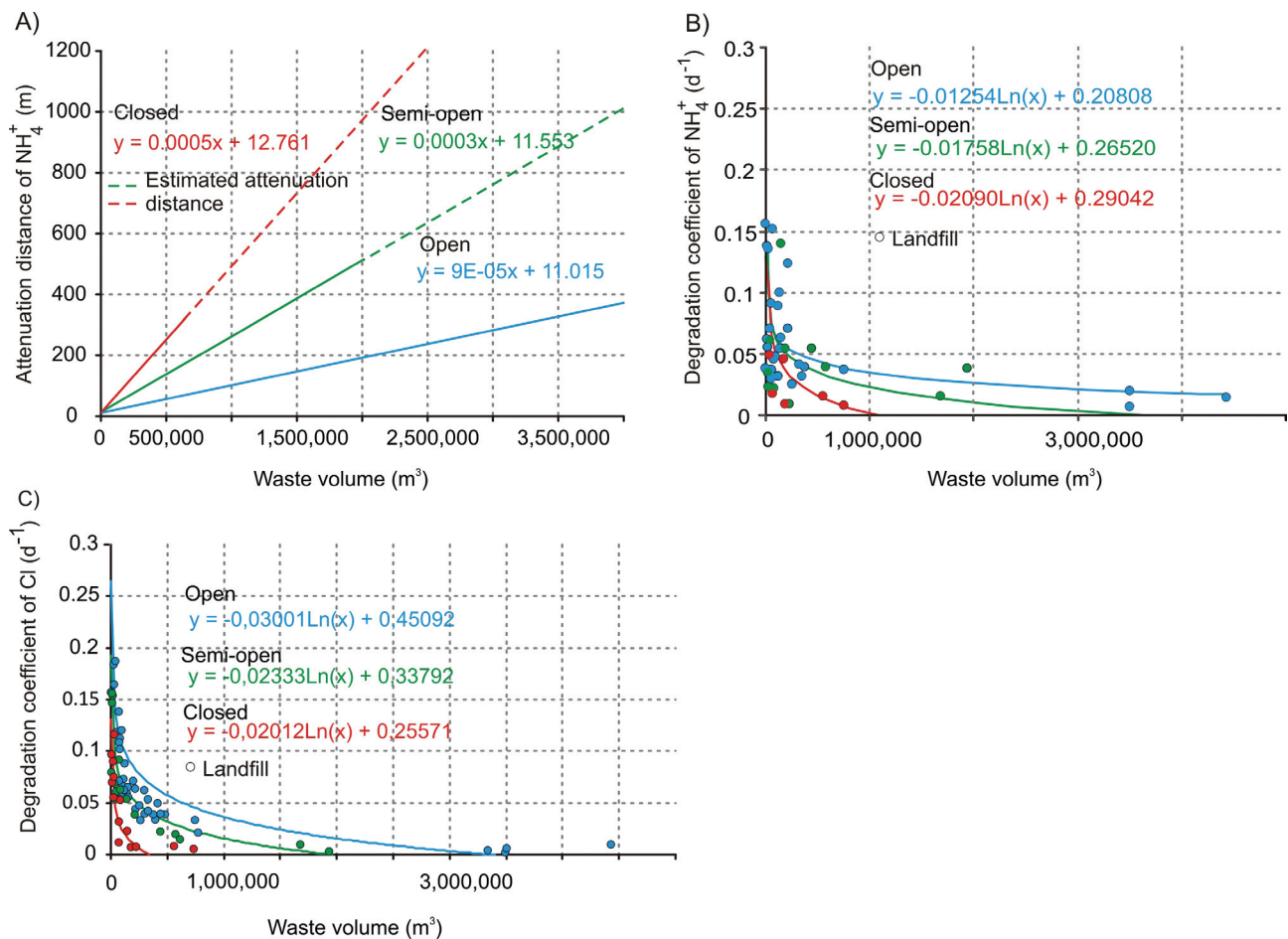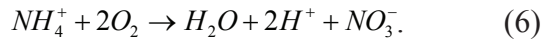

Fig. 4 Approximation curves of waste volume and attenuation distance of NH_4 (A), degradation coefficient of NH_4 (B), and degradation coefficient of Cl (C)

$$NH_4^+ + 2O_2 \rightarrow H_2O + 2H^+ + NO_3^-. \qquad (6)$$

The impact of dilution on the attenuation of NH_4^+, K^+ and Fe in open, semi-open and closed hydrogeological systems was represented by Cl^- degradation values. It was established that Cl^- degradation coefficient in the groundwater of open hydrogeological systems was about 66% higher than that in the groundwater of closed hydrogeological systems (Fig. 4C). This shows that the dilution attenuation capacity of NH_4^+, Fe and K^+ in open hydrogeological systems is significantly higher than that in closed hydrogeological systems. This trend is associated with higher hydraulic conductivity values characteristic of the deposits in open hydrogeological systems. It is known that dilution depends on specific aquifer factors, particularly hydraulic conductivity, hydraulic gradient and aquifer thickness (Lasagna *et al.* 2013). In addition, higher dilution intensity determines more intense hydraulic exchange and augmentation of the dissolved oxygen in groundwater (Huang *et al.* 2017). Therefore, in the groundwater of open hydrogeological systems more intense dilution processes were particularly important to the intensity of nitrification as well as oxidation and carbonate equilibrium of iron.

Figure 5 shows that with the increase of waste volume, degradation coefficients of NH_4^+ in the groundwater of all analysed hydrogeological systems decreased. The same decrease was noted in the degradation coefficient of Cl^-. This relationship between degradation coefficients of NH_4^+ and Cl^- shows that changes in NH_4^+ degradation and attenuation distances in groundwater were related to the differences in the intensity of hydrochemical and hydrodynamic processes in the degradation of NH_4^+ of various quantity.

According to the classification analysis of Cl^- degradation coefficients it was established that the highest dilution intensity in the groundwater of the analysed landfills was characteristic of landfill sites smaller than 30,000–90,000 m³. In the landfill sites of this size the quantity of NH_4^+ was up to 500 times lower than that of landfill sites larger than 305,000–600,000 m³ (Table 4). The mean NH_4^+ degradation coefficient in the groundwater of smaller landfills in open, semi-open and closed hydrogeological systems was 62–77%

Table 4 Waste volume limits which represent classification groups of Cl degradation coefficient, the mean values of NH_4, Fe and K attenuation distances, degradation coefficients and quantity

Hydrogeological system	Group of α of Cl^-, d^{-1}	Waste volume, m³	Fe			K^+			NH_4^+		
			X, m	α, d^{-1}	W, t	X, m	α, d^{-1}	W, t	X, m	α, d^{-1}	W, t
Open	>0.098	<60,400	55.9	0.044	0.502	22.59	0.091	13.21	6.82	0.075	4.82
	0.412–0.098	60,400–540,000	125.24	0.035	0.807	84.36	0.081	34.96	62.00	0.065	28.68
	<0.0412	>540,000	1,027	0.004	23.66	659.92	0.010	86.85	295.01	0.020	45.28
Semi-open	>0.053	<90,000	35.1	0.014	1.337	15.75	0.072	1.28	10.86	0.070	0.82
	0.014–0.053	90,000–600,000	407.31	0.010	6.670	212.64	0.030	25.29	105.81	0.059	34.76
	<0.014	>600,000	649.31	0.006	24.84	568.95	0.009	596.46	422.73	0.027	153.4
Closed	>0.040	<30,000			0.007	14.36	0.039	0.48	4.02	0.1	0.05
	0.011–0.040	30,000–305,000	461.74	0.007	1.116	188.37	0.011	22.85	87.73	0.050	21.31
	<0.011	>305,000	750.4	0.003	6.78	373.58	0.007	31.69	323.53	0.012	26.20

α degradation coefficient of a chemical parameter, *X* attenuation distance of a chemical parameter, *W* quantity of a chemical parameter.
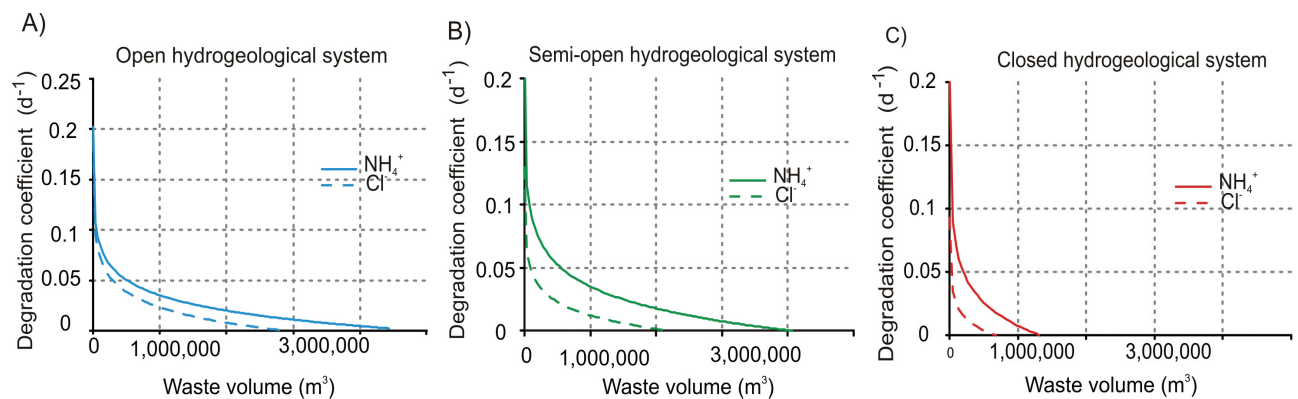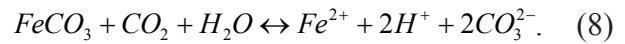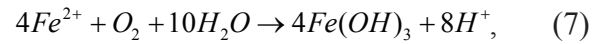

Fig. 5 Approximation curves of Cl and NH_4 degradation coefficients in the groundwater of open (A), semi-open (B) and closed (C) hydrogeological systems

higher than that in groundwater in larger landfills. Thus, due to higher dilution and nitrification intensity in smaller landfills, the mean NH_4^+ attenuation distance in groundwater was about 98–99% shorter than in larger landfills (Table 4). NH_4^+ sorption also played an important role (Belkhiri *et al.* 2012). In addition, higher dilution and nitrification intensity in smaller landfills determined a relatively smaller difference between the mean attenuation distance of NH_4^+ in groundwater in open and closed hydrogeological systems. This difference was about 95% smaller than in larger landfills. Increase in the difference of attenuation distances was related to a more stable increase in attenuation distances of NH_4^+ in groundwater in open hydrogeological systems and to a less stable increase in attenuation distances of NH_4^+ in closed hydrogeological systems. A more stable increase in attenuation distances of NH_4^+ in groundwater in open hydrogeological systems was determined by the regular inflow of oxygen and, due to favourable filtration properties, sufficiently intensive dilution effects even in the degradation of NH_4^+ of large quantity. In the meantime, in groundwater of closed hydrogeological systems, due to limited amount of oxygen, low attenuation capacity of dilution, and increasing level of contamination with NH_4^+, nitrification intensity constantly decreased with the increase of waste volume.

In the groundwater of open hydrogeological systems the mean attenuation distance of Fe was about 56% shorter and the mean degradation coefficient was about 90% higher than those in closed hydrogeological systems (Fig. 6).

This trend, despite the effect of a more intensive dilution process, was related to the prevailing more favourable oxidation conditions in the groundwater of open hydrogeological systems, more intensive iron oxidation (Eq. (7)), and a weaker carbonate equilibrium of iron along the flow line (Eq. (8)) than in semi-open and closed hydrogeological systems:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+, \quad (7)$$

$$FeCO_3 + CO_2 + H_2O \leftrightarrow Fe^{2+} + 2H^+ + 2CO_3^{2-}. \quad (8)$$

A continuous supply of oxygen along the flow line in the groundwater of open hydrogeological systems provides favourable conditions for the oxidation of organic matter. Small quantities of carbon dioxide are not conducive to intensive iron carbonate dissolution and accumulation of Fe^{+2} (Eq. (8)). Therefore, groundwater in open hydrogeological systems is usually weakly saturated or in the state of equilibrium with respect to iron carbonate minerals along the flow line (Belkhiri *et al.* 2012; Navarro, Carbonell 2008; Sajil Kumar, James 2016). With the improvement of oxidation conditions in groundwater, Fe^{+2} quickly precipitated (Van Breukelen *et al.* 2004). Meanwhile in the groundwater of semi-open and closed hydrogeological systems, due to low oxygen content, the destruction of organic matter is slow, a larger amount of CO_2 is emitted resulting in the most intensive dissolution of iron carbonates and increasing Fe^{+2} concentrations in groundwater (Christensen *et al.* 2001). In the groundwater of semi-open and closed hydrogeological systems, high saturation index values dominate. This supersaturation with respect to iron carbonates is caused by extremely slow iron carbonate precipitation kinetics (Christensen *et al.* 2001; Van Breukelen *et al.* 2004). These processes clearly extended the attenuation distances of iron in groundwater in semi-open and closed hydrogeological systems.

The relationship between Cl^- degradation coefficient and Fe degradation coefficient is related to changes in iron carbonate equilibrium. As can be seen from Fig. 7, in the groundwater of analysed hydrogeological systems iron degradation coefficients were about 67% lower than Cl^- degradation coefficients, although iron degradation together with the dilution process are intensified by iron oxidation and sorption
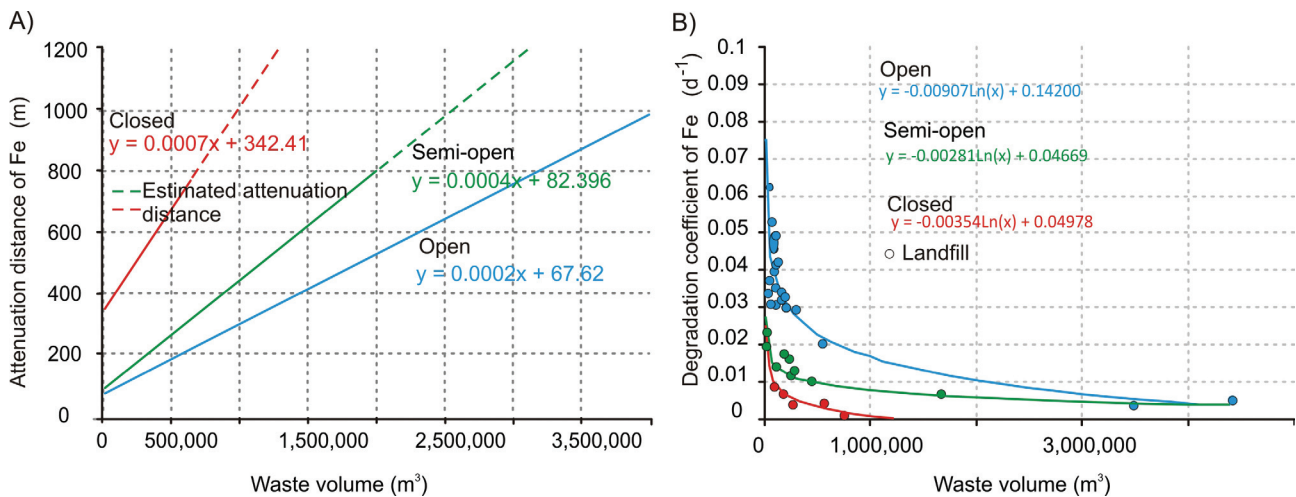

Fig. 6 Approximation curves of waste volume and attenuation distance of Fe (A) and degradation coefficient of Fe (B)

processes. This is because, due to dissolution of iron carbonates, groundwater is constantly supplemented with Fe ions. As a result, the values of iron degradation coefficient decrease. In addition, this may also be related to the complexation of Fe^{+2} with organic ligands. Because of the formation of these complexes, Fe^{+2} oxidation in the aerobic environment effectively decreases facilitating Fe^{+2} migration in groundwater along the flow line (Christensen *et al.* 2001).

In the groundwater of smaller landfills, the quantity of Fe was up to 1,000 times lower than that in the groundwater of larger landfills, and it consequently determined a higher intensity of iron oxidation and dilution processes. Hence, due to a small amount of organic matter and CO_2 emissions, dissolution of carbonate rock was weak. In groundwater in semi-open and closed hydrogeological systems, iron degradation was additionally intensified by sorption processes. It is known that iron is the most easily absorbed chemical parameter (Appelo, Postma 2005). These reasons determined that the mean iron degradation coefficient in the groundwater of smaller landfills of open, semi-open and closed hydrogeological systems was by 37–90% higher than in the groundwater of larger landfills. In the groundwater of smaller landfills the mean attenuation distance of iron was about 38–95% shorter than that in larger landfills (Table 4).

In the groundwater of smaller landfills the difference between the mean Fe attenuation distance in open hydrogeological systems and in closed hydrogeological systems was about 93% lower than the difference in larger landfills. Like in the case of NH_4^+, the increase in the difference of attenuation distances of Fe was related to a more stable increase of Fe attenuation distances in open hydrogeological systems and less stable Fe attenuation distances in closed hydrogeological systems. The said stability in open hydrogeological systems was determined by good oxygen capacity of aquifer, intensive iron oxidation processes and less intensive carbonate equilibrium processes even where large quantities of pollutants

were degrading. In the meantime, in the groundwater of closed hydrogeological systems, due to a limited amount of oxygen, small attenuation capacity of dilution, and increasing Fe contamination level, iron oxidation intensity declined with increasing waste volume. Furthermore, due to increase in organic matter and CO_2, iron carbonates were intensively dissolved.

In the groundwater of open hydrogeological systems, the mean attenuation distance of K^+ was 14% shorter and the mean degradation coefficient was about 79% higher than in closed hydrogeological systems (Fig. 8).

The identified trend was related to a more intensive dilution effect on K^+ degradation in the groundwater of open hydrogeological system than in semi-open and closed hydrogeological systems. It is known that dilution controls K^+ attenuation in sandy deposits, and dilution and sorption processes control K^+ attenuation in clayey deposits. Correspondingly, in this study, the relationship between Cl^- degradation and K^+ degradation coefficients has shown that the dilution process is the main factor which controls K^+ attenuation distances in groundwater (Fig. 9). It is known that Cl^- has an extremely low sorption capacity (Apello, Postma 2005).

In the groundwater of smaller landfills the quantity of K^+ was up to 500 times lower than that in the groundwater of larger landfills and, consequently, determined a greater dilution intensity. In the groundwater of open hydrogeological systems the mean degradation coefficient of potassium was about 83–89% higher than that in larger landfills. The difference of the mean K^+ attenuation distance in the groundwater of larger landfills in open and closed hydrogeological systems was about 96–67% lower than the said difference in larger landfills (Table 4).

CONCLUSIONS

The waste volume of landfills determines the quantity of the leachate entering the groundwater.
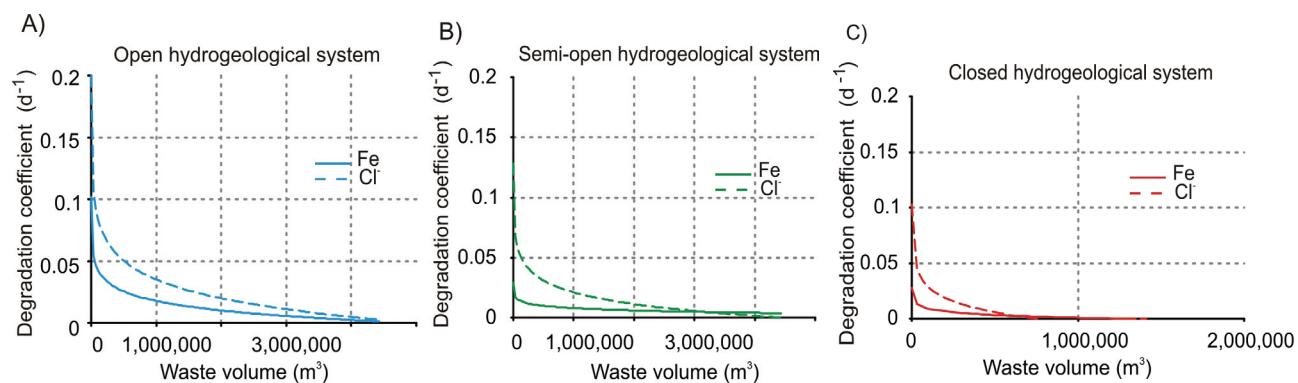

Fig. 7 Approximation curves of Cl and Fe degradation coefficients in the groundwater of open (A), semi-open (B) and closed (C) hydrogeological systems
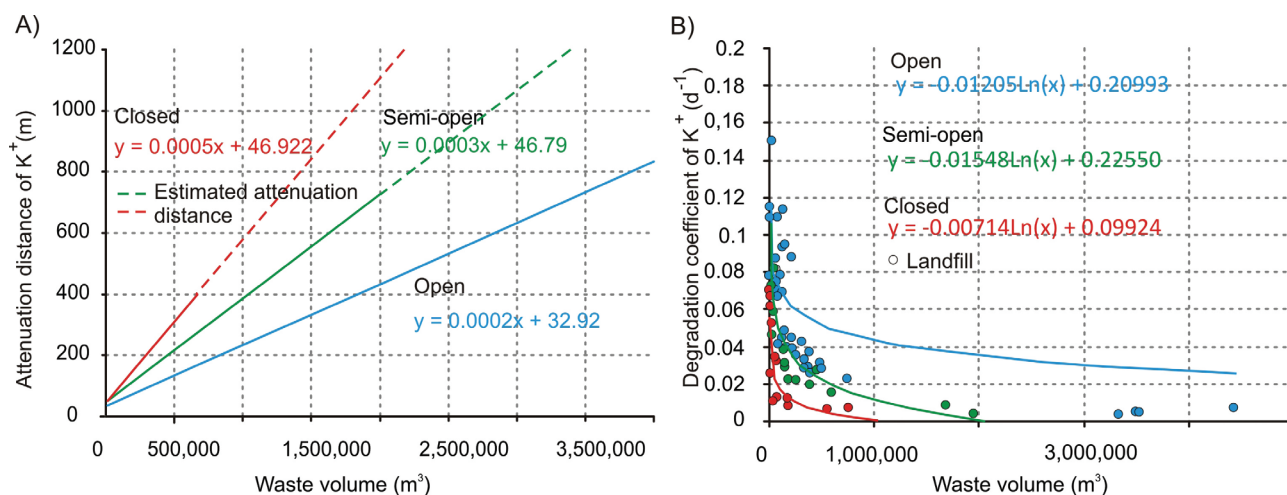
Fig. 8 Approximation curves of waste volume and attenuation distance of K (A) and degradation coefficient of K (B)
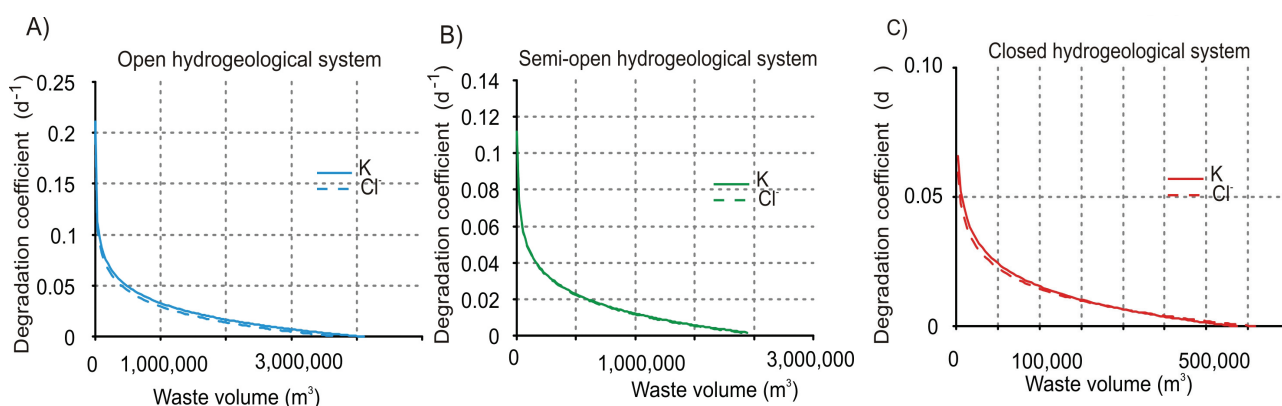

Fig. 9 Approximation curves of Cl and K degradation coefficients in the groundwater of open (A), semi-open (B) and closed (C) hydrogeological systems

The results of this study showed that according to the volume of waste, the study landfills can be divided into five categories: very small landfills ($<40,000$ m^3), small landfills ($40,000$–$100,000$ m^3), medium landfills ($100,000$–$300,000$ m^3), large landfills ($300,000$–$1,000,000$ m^3) and very large landfills ($>1,000,000$ m^3). Very small landfills make up the majority of the landfills.

Of all the studied inorganic chemical parameters, the groundwater of the study landfill sites was polluted to the highest degree with NH_4^+, Fe and K^+. Therefore, the impact of hydrochemical and hydrodynamic processes on the relationship between the waste volume and attenuation distance of these parameters was determined. The mean attenuation distances for NH_4^+, Fe and K^+ in groundwater ranged within 75–287 m, 76–365 m and 93–659 m, respectively, in open, semi-open and closed hydrogeological systems.

The approximation between the waste volume and attenuation distance showed that irrespective of waste volume, the degradation coefficients of NH_4^+, K^+ and Fe were by 36–90% higher in the groundwater of open hydrogeological systems, where attenuation distances were by 14–56% shorter compared with those in closed hydrogeological systems. Such a pattern was determined by the more intensive processes of nitrification, iron oxidation, dilution and less intensive changes in carbonate equilibrium in groundwater along the flow path in the open hydrogeological system.

In the analysed hydrogeological systems the degradation coefficients of NH_4^+, K^+ and Fe^+ in the groundwater of very small and small landfills were by 37–90% higher and attenuation distances were by 38–99% shorter compared with those in the groundwater of large and very large landfills. Also, in the groundwater of very small and small waste volume landfills the difference between NH_4^+, Fe and K^+ attenuation distance in open hydrogeological systems and in closed hydrogeological systems was about 89–97% lower than the difference in large and very large landfills. This pattern was related to the differences in the intensity of hydrochemical and hydrodynamic processes in the degradation of NH_4^+, K^+ and Fe^+ of various quantities.

The study may be used as a representative basis for the identification of attenuation distances in groundwater for other chemical parameters. The ob-

tained findings may also be used for the calibration of mathematical models of pollution migration in groundwater, to predict the dispersion of pollution in groundwater and to facilitate the selection of preventive measures for the reduction of groundwater pollution in the surroundings of landfills located in similar hydrogeological systems.

ACKNOWLEDGMENTS

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