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ASSESSMENT OF THE IMPACT OF BANJALUKA LANDFILL ON GROUNDWATER QUALITY

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Abstract: This study focuses on the analyses of the effects of solid waste landfill and their leachate on the groundwater quality in Banjaluka, Bosnia and Hercegovina. Leachates from municipal solid waste landfill contain a diversity of contaminants. Samples of landfill leachate and groundwater were analysed in order to evaluate the impact of leachate on groundwater quality from Banjaluka landfill. The leachate from Banjaluka landfill contains heavy metals, organic and inorganic compounds in its composition. Groundwater samples, which are under the influence of landfill, have higher values for heavy metals (Pb i Cd) than is proposed by the World Health Organization drinking water regulation and EU Directive on the quality of water intended for human consumption. The multivariate statistical methods, hierarchical cluster analysis and principal component analysis, were applied to groundwater and leachate physico-chemical data. Principal component analysis revealed two sources of pollution in the groundwater: first source is from natural/geochemical process in soil and groundwater and the second source of pollution is from landfill site and leachate. Hierarchical cluster analysis shows that one group represents the samples of groundwater under the influence of landfill while the second cluster represents samples of groundwater without impact of landfill site and leachate.

Keywords: landfill leachate, groundwater, pollution, principal component analysis, cluster analysis

1. INTRODUCTION

Landfilling is the simplest, cheapest and most cost effective method of disposing of waste (Hossain et al., 2014). If leachate infiltrates into the surrounding subsurface environment through the solid waste and liner materials, it could have potential negative effects on human health and environment. (Narayana, 2009; Pablos et al., 2011; Pearce et al., 2011). Leachate are highly concentrated complex effluents which contain dissolved organic matters, inorganic compounds such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides, and heavy metals such as cadmium, chromium, copper, lead, zinc, nickel, and xenobiotic organic substances (Niloufer et al., 2013; Hossain et al., 2014). Leachate contains a host of toxic and carcinogenic chemicals (e.g. polycyclic aromatic hydrocarbons, phthalates, halogenated aliphatic and aromatic compounds), which may cause harm to both humans and environment (Alslaibi et al., 2013). Since most landfills were built without engineered liners and leachate collection system, the highest environmental impact is the risk of groundwater pollution (Kjeldsen et al., 2002).

The European Directive 1999/31/EC establishes the control and monitoring procedures in the operational and closing phases of landfill. According to this Directive regulatory requirements include the measures intended to prevent surface and groundwater contamination by landfills (Directive, 1999). Assessment of groundwater contamination by landfills have been proposed by some authors using different methodologies, such as mathematical modelling like MODFLOW, FEFLOW (Wycisk et al., 2006; Rădulescu, 2009; Han et al., 2014), analysing physico-chemical composition of landfill leachate and groundwater (Reyeas-Lopez et al., 2008; Bandeira et al., 2008) and using multivariate statistical techniques (Mrklas et al., 2006; Talalaj & Dzienis, 2007; Singh et al., 2008).

The aim of this study is to investigate groundwater quality nearby Banjaluka landfill, Bosnia and Herzegovina (B&H). It was conducted by using multivariate statistical methods, hierarchical cluster analysis, and principal component analysis. Since 2012, monitoring of groundwater near the landfill was established, incited by residential buildings nearby. In this region, there is a frequent usage of groundwater from the wells within the households, for the purposes of supplying of water for drinking, irrigation and watering livestock.

2. MATERIAL AND METHODS

2.1. Study area

The city of Banjaluka is located in the north-western part of Bosnia and Hercegovina (B&H). Banjaluka is the university, economic, finance, political and administrative center of the Republic of Srpska (RS) and one of the two entities in Bosnia and Hercegovina (B&H). The city is located at latitude 44.78° N and longitude 17.19°E.

Banjaluka has a continental climate, with harsh winters and warm summers. The warmest month of the year is July, with an average temperature of 21.3°C. The coldest month of the year is January, when temperatures average near freezing at 0.8°C. Annual precipitation for Banjaluka is about 988 millimetres.

About 390 000 inhabitants live in Banjaluka region and 78% of the population is covered with waste collection and disposal system. Since there is no primary or secondary selection of waste, it all ends up on landfill without any recycling. The landfill is 10 km away from the city centre. Banjaluka landfill is used for disposal of municipal solid waste and non-hazardous waste since 1976 for the city of Banjaluka. In 2004 it became regional landfill, which, beside Banjaluka, includes seven municipalities from the region. This landfill is semi-controlled landfill constructed without an impermeable liner of compacted clay and geosynthetic material. This landfill is designated site where the dumped waste is compacted and a topsoil cover is provided daily to prevent odour nuisances. At Banjaluka landfill municipal, industrial (non-hazardous) and clinical wastes are dumped without segregation. About 80% of leachate is collected. The rest, which is not collected, is filtered into groundwater and surface water.

The local geology in the area of this study is generally represented by Miocene marl, marl limestone and clay. The thickness of the Miocene deposits in the landfill area is over 100 meters. Permeability coefficient of marl-clay deposits is 10^{-8} m/s. In hydrogeological terms, the rock mass in the vicinity of the landfill are impermeable.

2.2. Sampling and analysis

Twenty-four samples, untreated leachate (LW) from Banjaluka landfill were used for this study. Samples were taken at the entrance of the basin used for waste water storage. Samples of leachate were collected once a month. Groundwater samples were collected from three piezometers quarterly, on the depth of 8 meters. Eight samples were taken from each piezometer, and 24 samples of groundwater were collected in total. Leachate and groundwater samples were collected from Banjaluka landfill from July 2012 to June 2014. Groundwater monitoring networks are designed with reference to minimal requirements of landfill Directive (Directive, 1999), with at least one measuring point in the groundwater inflow region and two in the outflow region. Figure 1 shows location of piezometers around the landfill. Piezometer 1 (GW1) is located upstream the landfill and piezometers 2 and 3 (GW2, GW3) are located downstream the landfill, in direction of groundwater stream. Samples of groundwater from piezometer 1 GW1 are marked as GW1-1 through GW1-8, from piezometer GW2 as GW2-1 through GW2-8 and from piezometer GW3, samples are marked as GW3-1 through GW3-8. For each sample, 13 parameters of water quality were analysed.

All samples were collected, preserved and analysed according to B&H standards (BAS) and Standard Methods for the Examination of Water and Wastewater (SMEWW, 2005): pH (BAS ISO 10523), conductivity (EC) (BAS EN 27888), Biochemical Oxygen Demand (BOD) (BAS ISO 5815-1), Chemical Oxygen Demand (COD) (BAS ISO 6060), nitrate and nitrite (SMEWW 19th 450- NO_3^-B, SMEWW 19th 450-NO_2^-B). Metals (cadmium, lead, and zinc) were analyzed by atomic absorption spectroscopy method. Manganese (Mn) and iron (Fe) were analysed by spectrophotometer (SMEWW 19th), while the content of sulphate and chloride in leachate were analysed by volumetric method.

2.3. Statistical analysis

The results obtained from testing of leachate and groundwater were presented in the form of range, arithmetic mean and standard deviation (SD) and further analysed using the Statistical Package for Social sciences (SPSS, 2010) version 17.0 software package and Canoco version 4.5 (ter Braak and Smilauer, 2002).

Pearson correlation analysis was applied to analyse and establish physico-chemical relationships of landfill leachate and groundwater. Multivariate data analysis is used to explore data structure with principal component analysis (PCA) and hierarchical cluster analysis (HCA).

3. RESULTS AND DISCUSSION

3.1. Leachate characteristics

The results of physical and chemical analyses of the leachate samples from Banjaluka landfill are presented in table 1.

Kjeldsen et al., (2002) and Chian & DeWalle (1976) investigated composition of landfill leachate depending on the age of the landfill and waste degradation. The pH of young leachate is less than 6.5, because during acid phase leachate have high concentration of compounds. In the later stabile methanogenic phase, the pH leachate increases. Therefore, old leachate shows fairly constant pH with little variations and it may range between 7.5 and 9. pH values of leachate from Banjaluka landfill were in the range of 7.54 to 8.53, which is characteristic for old landfill leachate. Alkalinity of the leachate could indicate landfill exploited from a long time (Pablos et al., 2011).

Conductivity is often used as another indicator of the abundance of dissolved inorganic compounds or total concentration of cations and anions. Kjeldsen et al., (2002) evaluated landfill leachate characteristics where the range of conductivity was from 2500 to 35000 μS/cm. Conductivity of the leachate from Banjaluka landfill was in the range of 3010 to 9600 μS/cm. The results of the current study was similar with Mikac et al., (1998) who evaluated leachate characteristics from landfill in Croatia. The values of conductivity were from 3600 to 13500 μS/cm. Mor et al., (2006) showed that leachate collected from Gazipur landfill (India) had high conductivity of 24500 μS/cm, and these values were higher than those found in the present study.

Values of BOD and COD characteristic for old leachate are in range from 20 to 550 mg/l and from 500 to 4500 mg/l, respectively (Kjeldsen et al., 2002; Slomcyznska & Slomczynski, 2004). In this study, the BOD values for leachate at landfill site were from 200 to 580 mg/l and COD values were from 1329 to 4619 mg/l, which is characteristic for old landfill leachate. Renou et al., (2008) presented leachate composition from different landfills. In this study, values of COD vary from 70900 mg/l for young leachate obtained from the Thessaloniki Greater Area (Greece) to 100 mg/l with sample from a more than 10-year old landfill near Marseille (France). The BOD/COD ratio describes the degree of biodegradation and is used to assess the age of landfill. In the study of Renou et al., (2008) BOD/COD ratio in old leachate was in the range of 0.01(for landfill in France) and 0.37 (for landfill in Estonia). The ratio BOD/COD for leachate samples from Banjaluka landfill was from 0.08 to 0.31, which is characteristic for old leachate.

The highest recorded concentration of nitrate and nitrite were 2.69mg/l and 2.38mg/l, respectively. Microbial decomposition of organic carbon influences many processes of the nitrogen cycle. Nitrogen concentration can decrease due to microbial utilization of nitrate compounds and denitrifying as ammonia gas (Bhalla et al., 2013).

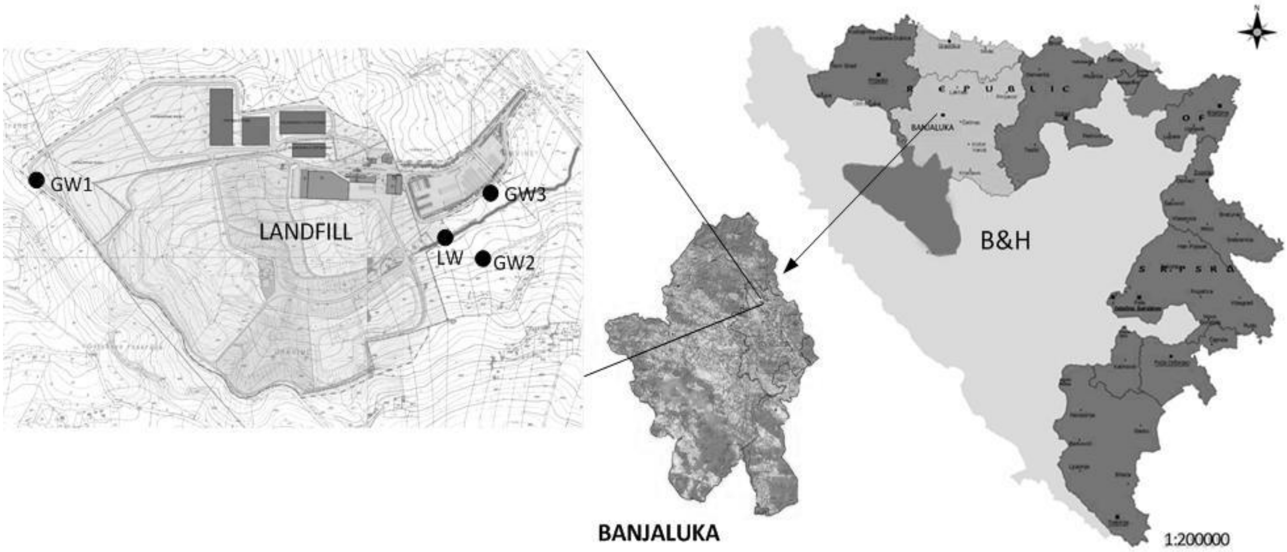

Figure 1. Location of study area

Kjeldsen et al., (2002) and Slomcyznska & Slomczynski, (2004) observed sulphate and chloride concentration in leachates from old landfills. Their studies showed that concentration of sulphate are usually between 10 and 420 mg/l and chloride from 15 to 4500 mg/l. Sulphate concentration in Banjaluka study was in the range from 334 to 491mg/l and is characteristic for old leachate. Sulphate concentration mostly depends on the level of decomposition of organic matter in waste and reduction of sulphate to sulphide (Kjeldsen et al., 2002, Chian & DeWalle, 1976). Sulphide then precipitates with various metals. Chloride concentration from Banjaluka landfill leachate was in the range of 309 to 425 mg/l which is characteristic for this parameter in old leachate.

Table 1. Physico-chemical composition of leachate from Banjaluka landfill.

	Unit	Landfill leachate	
		Range	Mean ± SD
pH	-	7.54-8.53	7.88±0.21
EC	μS/cm	3010-9600	4666.89±1533.10
BOD	mg/l	200-580	402.20±106.60
COD	mg/l	1329-4619	25889.59±969.61
Nitrate	mg/l	0.8-2.69	1.37±0.43
Nitrite	mg/l	0.92-2.38	1.60±0.43
BOD/COD	-	0.08-0.31	-
Chloride	mg/l	309-425	359.75±42.08
Sulphate	mg/l	334-491	424.51±60.34
Cadmium	mg/l	0.01-0.02	0.013±0.003
Iron	mg/l	2.07-6.07	3.95±1.48
Manganese	mg/l	0.54-0.81	0.63±0.11
Lead	mg/l	0.007-0.010	0.009±0.001
Zinc	mg/l	0.022-0.056	0.038±0.012

Concentration of iron and manganese were low and ranged from 2.07 to 6.07mg/l and from 0.53 to 0.81mg/l, respectively. Concentration of zinc in leachate from old landfill is between 0.03-4.0mg/l (Kjeldsen et al., 2002). Concentration of zinc for Banjaluka leachate was in range of 0.02 to 0.06 mg/l, which is characteristic for old leachate. Concentration of cadmium and lead in Banjaluka landfill leachate had values from 0.01 to 0.017mg/l and 0.007 to 0.01mg/l, respectively. As a result of decreased pH at methanogenic phase, a decrease in metal solubility occurs resulting in rapid decrease in concentration of heavy metals in leachate (Bhalla et al., 2013). High concentrations of Cd, Pb and Zn in leachate suggest that the wastes are mainly of municipal origin containing disposed of batteries, paint products, metallic items and fluorescents lamps (Kale et al., 2010).

The results with relatively high pH, alkalinity, low concentration BOD and COD in all the leachate samples analysed confirm the methanogenic condition of landfill, which are characteristic for old leachate.

3.2. Groundwater characteristics

The results of physical and chemical analyses for groundwater are given in table 2 with Republic of Srpska (RS) rulebook on health safety of drinking water ("Official Gazette of RS", No. 40/03). Our results show that the mean pH value in piezometer GW1, which is outside of the influence zone, was 7.10, while the average pH values in piezometers GW2 and GW3, which are in the influence zone of landfill, had slightly higher values, 7.23 and 7.27. These results of pH values are in agreement with the range values of 6.5 to 9.5 proposed by WHO (WHO, 2011) which is required for drinking water.

Electrical conductivity (EC) is the indicator of dissolved inorganic ions in groundwater. EC in the studied area are in the range between 950 and 1400 μS/cm, and are acceptable upper limits of 2500 μS/cm for EU directive on the quality of water intended for human consumption (Directive, 1998). Average values of electrical conductivity in piezometers GW2 and GW3 were 1209.37 and 1111.75 μS/cm, respectively, and those values were slightly higher than in piezometer GW1 (mean 1043.13 μS/cm). Mor et al., (2006) investigated ground water quality near municipal landfill at Gazipur, Delhi (India) and their results also showed neutral pH values of groundwater (range 7.02-7.85) and EC was found to be high (range 617-3620 μS/cm). These high conductivity values obtained for the groundwater near landfill is an indication of its effect on the water quality (Mor et al., 2006).

The mean BOD and COD concentrations of three monitoring wells ranged between 3-85 mg/l for BOD and 15-125 mg/l for COD. This indicates that there is organic contamination from landfill and leachate to the groundwater surrounding the site, because groundwater contains little or no organic matter. This has also been found by Hube et al., (2011) who investigated the natural attenuation in groundwater near a landfill, in the central region of France, near the town of La Machine. COD values in the leachate ranged from 300 to 3000 mg/l while in the groundwater, COD values were in the range from 2 to 70 mg/l.

Nitrate concentrations were in the range from 0.5 to 25 mg/l, and nitrite from 0.01 to 0.50 mg/l. The low concentrations of these parameters for all groundwater samples were below the standard acceptable levels for drinking water as suggested by WHO (WHO, 2011) (nitrate 50 mg/l and nitrite 3 mg/l) and EU directive (Directive, 1998) (nitrate 50 mg/l and nitrite 0.5mg/l).

Maximum concentrations of chloride and sulphate (121.0 and 347.0mg/l) were not above limit required by WHO for quality of drinking water (WHO, 2011) (250 and 500mg/l). It is evident that concentrations of chloride and sulphate in piezometers GW2 and GW3, situated below the landfill, had far higher values than values in piezometer GW1, which is outside of landfill influence zone. It indicates that leachate landfill had an impact on the increase of concentration of these ions in groundwater below landfill.

Agricultural fertilizers and leachate are the main source of sulphate in groundwater (Kale et al., 2010). The major sources for nitrate in groundwater include domestic sewage, runoff from agricultural fields, and leachate from landfill sites.

Bahaa-eldin et al., (2010) investigated the effect of municipal landfill leachate on groundwater quality in Malaysia. Their results showed that the concentration of chloride (355.48mg/l), nitrate (10.40 mg/l) and nitrite (14.59mg/l) can be used as indicators of pollution of groundwater with leachate. Rapti-Caputo & Vaccaro (2006) studied the influence of landfill leachate on the chemical composition of aquifer system in Italy. In their study the pH values of groundwater were between 7.16 and 7.9, concentrations of chlorides ranged from 10.15 to 467.5 mg/l, nitrates from 1.9 to 166 mg/l and sulphates from 23 to 1128mg/l.

Allowed value of Cd in drinking water is 0.003 mg/l according to WHO (WHO, 2011) and 0.005 mg/l according to Directive EU (Directive, 1998). Concentration of Cd in samples of groundwater from Banjaluka was in the range of 0.001 to 0.1mg/l, and was exceeding allowed values. The high concentrations indicate that there will be some concerning human health risk caused by high intake of Cd (Han et al., 2014). Concentration of iron and manganese were in the range from 0.81 to 2.5 mg/l and from 0.95 to 3.20 mg/l, respectively. Mn and Fe may be present in samples as a naturally occurring constituent of groundwater from weathering of Fe and Mn bearing minerals and rocks.

Concentrations of Pb in samples groundwater (0.01 to 0.1mg/l) exceed the limits of 0.01mg/l (WHO, 2011; Directive, 1998). Possible sources of lead contamination may be batteries, photographs, old lead-based paints and lead pipes disposed at the landfill, which are toxic to all forms of life (Han et at., 2014). Mikac et al., (1998) investigated the groundwater contamination in the vicinity of a municipal solid waste landfill in Zagreb, Croatia. In their study concentration of Cd of groundwater were between 0.00001 and 0.00017mg/l, concentration of manganese ranged from 0.01 to 3.5mg/l, and iron from 0.03 to 120 mg/l. This results shows that the groundwater near Zagreb landfill is contaminated.

Concentration of Zn in samples of groundwater near Banjaluka landfill was in the range of 0.01 to 0.30 mg/l. The zinc concentration did not exceed the WHO standards (5 mg/l). The presence of zinc in the groundwater indicates that the landfill may be receiving waste batteries and fluorescent light bulbs (Han et al., 2014).

3.3. Statistical analysis

3.3.1. Correlations analysis

The relationship between various physico-chemical components of landfill leachate and groundwater were studied using Pearson correlation at the level of $p \leq 0.05$ and results are shown in Table 3 and Table 4. Correlation coefficient is often used as a simplified statistical tool to show the degree of dependency of one variable to the other (Kanade & Gaikwad, 2011).

Table 2. Physico-chemical analyses of groundwater near Banjaluka landfill, B&H (All values in mg/l except pH (in pH units) and conductivity (in µS/cm))

	GW1		GW2		GW3		Official Gazette of RS, No.40/03
	Mean±SD	Range	Mean±SD	Range	Mean±SD	Range	
pH	7.10±0.17	6.90-7.40	7.23±0.26	6.80-7.50	7.27±0.01	7.10-7.40	6.8-8.5
EC	1043.13±81.41	975-1200	1209.38±132.24	950-1400	1111.75±158.94	950-1289	1000
BOD	9.25±4.20	3.00-15.00	47.87±28.03	12-85	47.5±23.27	9-72	-
COD	22.25±5.75	15.00-30.00	71.87±21.67	30-98	82.63±22.28	52-125	-
Nitrate	0.67±0.15	0.50-0.90	13.5±4.40	8-22	17.13±4.29	12-25	50
Nitrite	0.02±0.008	0.01-0.03	0.25±0.13	0.10-0.50	0.32±.10	0.15-0.50	0.03
Chloride	7.93±1.66	5.00-10.00	68.25±34.77	12-121	61.88±32.46	15-102	200
Sulphate	36.81±6.53	27.00-44.20	230.63±65.12	128-329	294.5±35.43	250-347	250
Cd	0.007±0.003	0001-0.01	0.07±0.04	0.01-0.10	0.06±0.03	0.01-0.09	0.003
Fe	1.36±0.29	0.82-1.65	1.53±0.16	130-1.79	1.28±0.21	0.90-2.50	0.3
Mn	1.23±0.17	0.95-1.40	2.17±0.90	1.29-3.20	1.46±0.56	0.90-2.50	0.05
Pb	0.009±0.001	0.01-0.019	0.03±0.002	0.01-0.06	0.05±0.03	0.01-0.1	0.01
Zn	0.075±0.04	0.01-0.15	0.18±0.03	0.12-0.22	0.21±0.05	0.15-0.30	3

The results for landfill leachate showed the negative correlation of BOD with pH (r=-0.51) and EC (r=-0.64). Chloride in landfill leachate had a low negative correlation between Fe (r=-0.54) and Mn (r=-0.53) and positive correlation with Zn (r=0.52). Significant correlation in landfill leachate were between sulphate/Cd (r=-0.97), sulphate/Fe (r=0.75), sulphate/Mn (r=0.70), sulphate/Pb (r=0.65), Cd/Fe (r=-0.89), Cd/Mn (r=-0.62), Cd/Pb (r=-0.72) and Fe/Pb (r=0.72).

In groundwater samples BOD is in significant correlation with COD, nitrate, nitrite, chloride, sulphate and Zn, and COD has correlation between nitrate, nitrite, chloride, sulphate, Cd and Zn. Nitrate shows correlation with nitrate (r=0.82) and Zn (0.85), while chloride is correlated with sulphate (r=0.70) and Cd (r=0.66).

3.3.2. Hierarchical cluster analysis (HCA)

Cluster analysis is often used to group variables into clusters on the basis of similarities or dissimilarities so that each cluster represents a specific process in a system (Kanade & Gaikwad, 2011, Venkatramanan et al., 2014). The hierarchical cluster analysis (HCA) is a data classification technique that is widely applied in Earth sciences and often used in the classification of hydrogeochemical data (typically illustrated by dendrograms) (Guler et al., 2002, Kiurski et al., 2013). In this study, the HCA was applied to leachate and groundwater data from 3 different locations (one upstream and two downstream the landfill). A classifications scheme was using the Euclidean distance for similar measures.

Three main groups of clusters are visible on the dendrogram for groundwater samples (Fig. 2). On the basis of HCA divisions are as follows: Cluster 1 (GW1-1, GW1-2, GW1-3, GW1-4, GW1-5, GW1-6, GW1-7 i GW1-8), Cluster 2 (GW2-1, GW2-2, GW2-4, GW2-5, GW2-6, GW2-7, GW2-8, GW3-1, GW3-2, GW3-3, GW3-4, GW3-5, GW3-6, GW3-7 i GW3-8) i Cluster 3 (GW2-3). Stations of the same clusters have the similar pattern of the groundwater quality. Cluster 1 represents samples of groundwater from piezometer GW1, which is outside of zone of landfill influence.

Cluster 2 and Cluster 3 represent samples of groundwater from piezometers GW2 and GW3, which are in the zone of landfill influence. Cluster 2 represents samples of groundwater that are polluted by municipal solid waste and leachate. Cluster 3 represents the sample of groundwater GW2-3 which is moderately polluted.

Table 3. Correlation coefficients between measured parameters in landfill leachate samples

	pH	EC	BOD	COD	Nitrate	Nitrite	Chloride	Sulphate	Cd	Fe	Mn	Pb	Zn
pH	1.00												
EC	0.45	1.00											
BOD	**-0.51**	**-0.64**	1.00										
COD	0.23	0.41	-0.15	1.00									
Nitrate	0.16	0.23	-0.11	-0.01	1.00								
Nitrite	0.22	-0.05	-0.05	-0.05	-0.08	1.00							
Chloride	0.09	-0.06	-0.03	-0.08	-0.03	0.05	1.00						
Sulphate	-0.03	-0.02	0.12	0.13	-0.32	0.05	-0.18	1.00					
Cd	-0.04	-0.03	-0.10	-0.15	0.30	-0.12	0.32	**-0.97**	1.00				
Fe	0.16	0.12	0.07	0.16	-0.21	-0.08	**-0.54**	**0.75**	**-0.89**	1.00			
Mn	-0.30	-0.10	0.11	0.06	-0.19	-0.13	**-0.53**	**0.70**	**-0.62**	0.39	1.00		
Pb	0.21	0.03	0.07	0.22	-0.22	0.06	0.07	**0.65**	**-0.72**	**0.72**	0.03	1.00	
Zn	-0.01	-0.16	0.11	0.02	-0.20	0.14	**0.52**	0.24	-0.15	-0.05	-0.08	0.33	1.00

Correlation is significant at $p \leq 0.05$.

Table 4. Correlation coefficients between measured parameters in groundwater samples

	pH	EC	BOD	COD	Nitrate	Nitrite	Chloride	Sulphate	Cd	Fe	Mn	Pb	Zn
pH	1.00												
EC	0.37	1.00											
BOD	0.24	0.39	1.00										
COD	0.31	0.20	**0.54**	1.00									
Nitrate	0.33	0.28	**0.62**	**0.76**	1.00								
Nitrite	0.15	0.26	**0.54**	**0.63**	**0.82**	1.00							
Chloride	0.32	**0.50**	**0.53**	**0.74**	0.42	0.46	1.00						
Sulphate	0.45	0.36	**0.57**	**0.80**	0.33	0.48	**0.70**	1.00					
Cd	0.42	0.45	0.43	**0.58**	0.47	0.20	**0.66**	0.42	1.00				
Fe	-0.29	0.03	-0.04	0.08	-0.04	-0.01	0.20	-0.08	-0.01	1.00			
Mn	-0.14	-0.01	0.38	0.31	0.41	0.30	0.17	0.06	0.11	0.47	1.00		
Pb	0.26	0.45	0.25	0.22	0.43	0.21	0.37	0.43	0.53	-0.12	-0.05	1.00	
Zn	0.40	0.37	**0.57**	**0.67**	**0.85**	0.45	0.49	**0.81**	**0.59**	-0.22	0.14	**0.55**	1.00

Correlation is significant at $p \leq 0.05$.

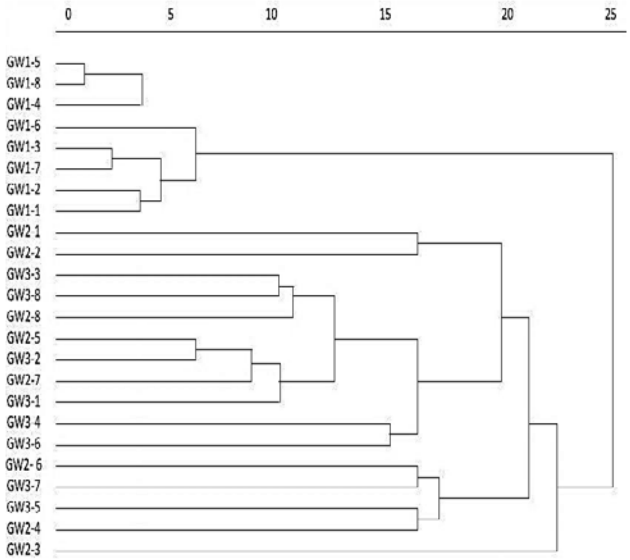

Figure 2. Dendrogram of the hierarchical cluster analysis for 24 groundwater samples

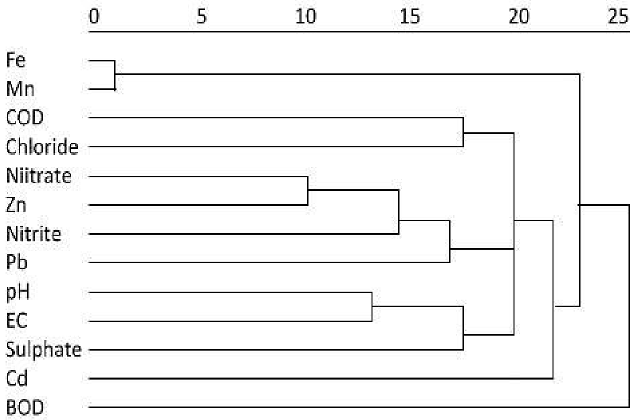

Figure 3. Dendrogram of the hierarchical cluster analysis of the groundwater quality

Singh et al., (2008) investigated groundwater quality near the municipal landfill in India, where they distinguished two clusters; first cluster represented the samples of groundwater under the influence of landfill while the second cluster represented the samples without the impact of landfill leachate.

Results of hierarchical cluster analyses of groundwater quality data are shown in figure 3. Water quality variables were grouped into cluster because of their physico-chemical association and similarity of coefficients. Cluster 1 contained pH, EC, COD, nitrate, nitrite, chloride, sulphate, Cd, Pb and Zn. Cluster 2 contained BOD and Cluster 3 contained Fe and Mn. Variables from Cluster 1 and 2 are superficial contribution indicator and water anthropogenic degradation. Cluster 1 and 2 shows that groundwater contain organic matter (BOD, COD), inorganic matters (nitrate, nitrite, chloride, sulphate), and heavy metals (Pb, Zn, Cd), which originates from leachate. Cluster 3 contains Mn and Fe, and may be present in samples as a naturally occurring constituent of groundwater.

3.3.3. Principal component analysis (PCA)

Principal component analysis is performed to reduce a large number of variables into a smaller number and for further investigation of the relationships between the elements. The principal components (PC) with Eigenvalues larger than 1 are extracted with the PC loadings rotated for the maximum variance (Batayneh & Zumlot, 2012). The results of the PCA based on three most significant PC indicate that these PC explain about 71% of total sample variance which is summarized in Table 5.

Table 5. Principal components analysis after rotation for chemical properties of groundwater samples

Parameters	PC1	PC2	PC3
Nitrate	**.931**	.209	.009
Nitrite	**.887**	.034	.044
Sulphate	**.820**	.444	-.120
Zn	**.791**	.399	-.214
COD	**.785**	.334	.165
BOD	**.657**	.312	.157
Cd	.328	**.784**	.024
EC	.089	**.777**	.030
Chloride	.436	**.695**	.272
Pb	.203	**.658**	-.189
pH	.230	**.515**	-.423
Fe	-.113	.073	**.887**
Mn	.397	-.109	**.734**
Initial eigenvalue	6.18	1.87	1.32
% of variance	47.16	14.41	10.16
Cumulative %	47.16	61.57	71.74

PC1 contributed 47.16% of the total variance and contained nitrate, nitrite, sulphate, Zn, COD and BOD and corresponds with Cluster 1 and 2. This PC1 seems to be attributed to anthropogenic sources, organic and inorganic matter in groundwater, which originates from leachate. PC2 accounts for 14.41% of the variance and contains Cd, EC, chloride, Pb and pH and corresponds with Cluster 1 and Cluster 2, and indicate that groundwater chemistry is largely influenced by the presence of landfill site and its leachate. PC3 accounts for 10.16% of the variance and contains Fe and Mn, and corresponds with Cluster 3. Mn and Fe may be present in samples as a naturally occurring constituent of groundwater from weathering of Fe and Mn bearing minerals and rocks.

PCA plot of physico-chemical parameters for groundwater is shown on figure 4. PCA is used to ordinate physic-chemical parameters with different groundwater samples. Physico-chemical variables in the diagram are represented by arrows, where the direction of arrows indicates the direction in which the variable increases most, and the length of the arrow represent the rate of change in that direction. Similar sites are on the graph placed in a vicinity of each other.

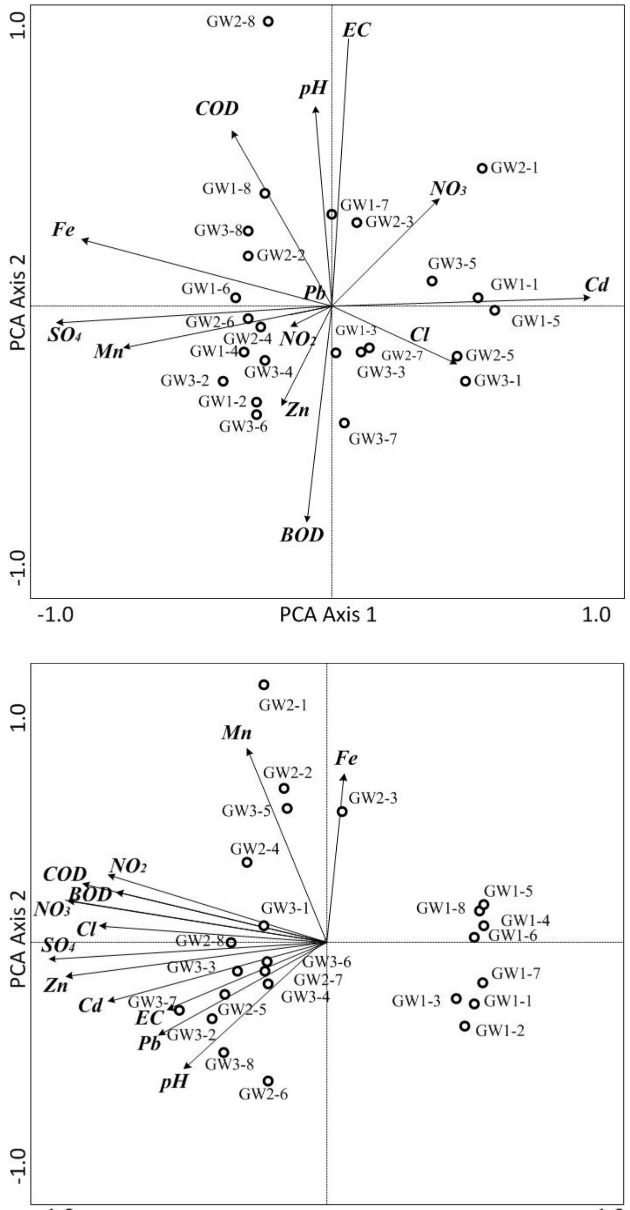

Figure 4. The loading plots for physico-chemical parameters in groundwater samples

PCA graph shows clear separation of different sites depending on the level of pollution. The first PCA axis separated sites on the basis of specific conductivity and other indicators of anthropogenic pollution while the second axis corresponded to Mn and Fe. Our results further show clear separation among different sites. Groundwater samples collected from piezometer GW 1, which is outside of the influence zone of the landfill all cluster in the first and second quadrant, and are characterised with low values for all measured parameters. On the other hand, samples collected from piezometers GW 1 and GW 3, which are in the influence of landfill, are clustered around higher values for measured physico-chemical parameters.

4. CONCLUSION

Landfill leachate has in its composition organic, inorganic compounds and heavy metals. Most of the analysed parameters of quality of groundwater had higher concentrations in piezometers which were in the zone of landfill influence, comparing to piezometer that was outside of the zone of landfill influence. The finding obtained from this study area is unreliable for drinking water supply purposes.

Heavy metals in all samples do indicate an empirical relation between landfill leachate and groundwater samples. Cluster analysis separates two groups of samples comprise samples with and without the influence of landfill and leachate. The results of principal component analysis indicate that an anthropogenic pollution source is dominated over natural process in the vicinity of landfill site. PCA results further show clear separation of the sites that are not influenced by the landfill site from those downstream the landfill, suggesting that landfill has considerable impact on the quality of groundwater.

It can be concluded that there is contamination of groundwater by seepage of landfill through the landfill soil, despite the fact that the rocks that are forming landfill terrain have low permeability. Some feasible options for improving groundwater quality are as follows: (1) It could be recommended to perform remediation of the landfill and to construct the sanitary landfill with a device for treatment of landfill leachate, which would prevent or reduce pollution from landfill into the environment. It is necessary to introduce stricter control inputs of waste to landfill, with the aim of preventing the disposal of hazardous waste (2) On the other hand, removing the waste from old landfill and hauling it to incineration plant or to another landfill, would be expensive (if feasible at all). (3) The only other proven technology for remediation of old landfill is the installation of an impermeable cap over the landfill preventing infiltration into the landfill and hence preventing the generation of leachate. (4) Increasing evapotranspiration rate by planting vegetation cover over the landfill in order to reduce leachate production. (5) Close the landfill. This would prevent emission of pollution in groundwater and reduce the risk to the health of the population in the vicinity of the landfill that are using wells for water supply and irrigation. The results from this study support the need for continuous monitoring of the groundwater.

REFERENCES

Alslaibi T.M., Abustan I., Mogheir Y.K. & Afifi S., 2013. *Quantification of leachate discharged to groundwater using the water balance method and the Hydrologic Evaluation of Landfill Performance (HELP) model*. Waste Management & Research, 31 (1), 50-59.

Bahaa-eldin E.A.R., Yusoff I., Samsudin A.R., Yaacob W.Z.W. & Rafek A.G.M., 2010. *Deterioration of groundwater quality in the vicinity of an active open-tipping site in West Malaysia.* Hydrogeology Journal, 18, 997-1006.

Bandeira J.V., Mingote R.M., Baptista M.B., Oliveira D.M. & Lima F.P., 2008. *The use of tritium content as an indicator of the groundwater contamination by sanitary landfills leachate in the region of Belo Horizonte City, Brazil.* Water Science Technology, 57, 1915-1920.

Batayneh A. & Zumlot T., 2012. *Multivariate statistical approach to geochemical method in water quality factor identification; Application to the Shallow aquifer system of the Yarmouk.* Research Journal of Environmental and Earth Sciences, 7, 756-768.

Bhalla B., Saini M.S. & Jha M.K., 2013. *Effect of age and seasonal variations on leachate characteristics of municipal solid waste landfill.* International Journal of Research in Engineering and Technology, 2, 223-232.

ter Braak C.J.F. & Smilauer P., 2002. *CANOCO reference manual and CanoDraw for Windows user's guide: software for canonical community ordination (version 4.5).* Microcomputer Power, Ithaca, New York, 500p.

Chian E.S.K. & DeWalle, F.B., 1976. *Sanitary landfill leachates and their treatment.* Journal of the Environmental Engineering Division, 411-431.

European Council, 1999. *European Council Directive 1999/31/EC of 26 April 1999 on the landfill waste.* Official Journal of the European Communities, Brussels, Belgium.

European Council, 1998. *European Council Directive 98/83/EC on the quality of water intended for human consumption.* Official Journal of the European Communities, Brussels.

Han D., Tong X., Currell M.J., Cao G., Jin M. & Tong C., 2014. *Evaluation of the impact of an uncontrolled landfill on surrounding groundwater quality, Zhoukou*, China. Journal of Geochemical Exploration 136, 24-39.

Hossain L., Das S.R. & Hossain M.K., 2014. *Impact of landfill leachate on surface and groundwater quality*. Journal of Environmental Science and Technology 7(6), 337-346.

Hube D., Gourcy L., Gourry J.C. & Guyonnet., 2011. *Investigations of natural attenuation in groundwater near a landfill and implications for landfill post-closure.* Waste Management & Research 29 (1), 77-88.

Guler C., Thyne G., McCray J. & Turner K., 2002. *Evaluation of graphical and multivariate statistical methods for classification of water chemistry data.* Hydrogeology Journal, 10 (4), 455-474.

Kale S.S., Kadam A.K., Kumar S. & Pawar N.J., 2010. *Evaluating pollution potential of leachate from landfill site, from the Pune metropolitan city and its impact on shallow basaltic aquifers.* Environmental Monitoring and Assessment, 162, 327-346.

Kanade S.B. & Gaikwad V.B., 2011. *A multivariate statistical analysis of bore well chemistry data - Nashik and Niphad taluka of Maharashtra, India.* Universal Journal of Environmental Research and Technology. 1, 193-202.

Kiurski J.S., Oros I.B., Ralevic N.M., Kovacevic I.M., Adamovic S.Z., Krstic J.D. & Comic L.LJ., 2013, *Cluster and principal component analysis in the assessment of fountain solution quality.* Carpathian Journal of Earth and Environmental Sciences, 8(1), 19-28.

Kjeldsen P., Barlaz M., Rooker A., Baun A., Ledin A., & Christensen T., 2002. *Present and long-term composition of MSW landfill leachate: A review.* Critical reviews in Environmental Science and Technology, 32 (4), 297-336.

Mikac N., Cosovic B., Ahel M., Andreis S. & Toncic Z., 1998. *Assessment of groundwater contamination in the vicinity of a municipal solid waste landfill (Zagreb, Croatia).* Water Science and Technology 37, 37-44.

Mor S., Ravindra K., Dahiya R.P. & Chandra A., 2006. *Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site.* Environmental Monitoring and Assessment, 118,435-456.

Mrklas O., Bentley L.R., Lunn S.R.D. & Chu A., 2006. *Principal component analyses of groundwater chemistry data during enhanced bioremediation.* Water, Air and Soil Pollution, 169, 395-411.

Narayana T., 2009. *Municipal solid waste management in India: From waste disposal to recovery of resources?.* Waste Management, 29, 1163-1166.

Niloufer S., Swamy A.V.V.S. & Devi K.S., 2013. *Ground water quality in the vicinity of municipal solid waste dump sites in Vijayawda, A.P.* International Journal of Engineering & Science Research 3(8), 419-425.

Pablos M.V., Martini F., Fernandez C., Babin M.M., Herraez I., Miranda J., Martinez J., Carbonell G., San-Segundo L., Garcia-Hortiguela P. & Tarazona J.V., 2011. *Correlation between physicochemical and ekotoxicological approaches to estimate landfill leachates toxicity.* Waste Management, 31, 1841-1847.

Pearce A.R., Rizzo D.M. & Mouser P.J., 2011. *Subsurface characterization of groundwater contaminated by landfill leachate using microbial community profile data and a nonparametric decision-making process.* Water Resources Research, 47 (6).

Radulescu M., 2009. *Evolution of a groundwater contaminating plume originating from tar waste – current conditions and remedial strategies.* Carpathian Journal of Earth and Environmental Sciences, 4(1), 5-18.

Rapti-Caputo D. & Vaccaro C., 2006. *Geochemical evidences of landfill leachate in groundwater.* Engineering Geology, 85, 111-121.

Renou S., Givaudan J.G., Poulain S., Dirassouyan F. & Moulin P., 2008. *Landfill leachate treatment: Review and opportunity.* Journal of Hazardous Materials, 150, 468-493.

Reyeas-Lopez J.A., Ramirez-Hernandez J., Lazaro-Mancilla O., Carreon-Diazeonti C. & Garrdio M.M.L., 2008. *Assessment of groundwater contamination by landfill leachate: a case in Mexico*. Waste Management, 28, 33-39.

Official Gazette of Republic of Srpska, No 40/03, 2003. *Rulebook on health safety of drinking water*, Ministry of Health and Social Welfare of the Republic of Srpska.

Singh U.K., Kumar M., Chauhan R., Jha P.K., Ramanathan A.L. & Subramanian V., 2008. *Assessment of the impact of landfill on groundwater quality: A case study of the Pirana site in western India.* Environmental Monitoring and Assessment, 141, 309-321.

Slomcyznska B. & Slomczynski T., 2004. *Physico-chemical and toxicological characteristics of leachates from MSW landfills.* Polish Journal of Environmental Studies, 13, 627-637

SMEWW, (2005). 21th edn, *Standard Methods for the Examination of Water and Wastewater,* Water Environment Federation, Portland Press Ltd., London.

SPSS-17, 2010. *Statistical Package for the Social Sciences.* SPSS Inc. Chicago, USA.

Talalaj I.A. & Dzienis L., 2007. *Influence of leachate on quality of underground waters.* Polish Journal of Environmental Studies, 16, 139-144.

Venkatramanan S., Chung S.Y., Lee S.Y. & Park N., 2014. *Assessment of river water quality via environmentric multivariate statistical tools and water quality index: A case study of Nakdong River Basin, Korea.* Carpathian Journal of Earth and Environmental Sciences, 9(2): 125-132.

WHO (World Health Organization), 2011. *Guideline for drinking water quality 4th edition*, Geneva, World Health Organization, 307-43.

Wycisk P., Steinmetz T., Neumann C.H., Gossel W. & Weiss H., 2006. *Exposure route assessment of groundwater pollutants from multi-source contaminated mega sites - a case study Oslo.* Organohalogen compounds (26th International Symposium on halogenated persistent organic pollutants), 68.

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