

RESEARCH ARTICLE

Environmental Chemistry

Characterization of landfill leachate at the Karadiyana open dumpsite, Sri Lanka, and assessment of water pollution in its vicinity

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Submitted: 23 December 2020; Revised: 24 May 2021; Accepted: 24 September 2021

Abstract: Contamination of ground and surface waters by landfill leachate is a prime environmental concern. The present research assesses chemical composition of leachate generated in the Karadiyana open dumpsite in Sri Lanka and the groundwater pollution caused by the landfill. The leachate pollution index (LPI) of Karadiyana is 34.00, suggesting that it has the potential to contaminate the environment. The nitrate, ammonia, and total phosphate concentrations in leachate varied in the range of 20.70 to 167.80, 376.55 to 580.33 and 10.00 to 84.00 mg/L respectively. Four major groups, namely, tryptophan- and tyrosine-like protein fractions, and fulvic and humic fractions were identified in leachate using fluorescence data. The bio chemical oxygen demand (BOD) to chemical oxygen demand (COD) ratio of leachate in the present study varied between 0.39 and 0.49 which categorizes leachate into intermediate age with medium biodegradability. This observation was further verified by the average pH and COD values of leachate; 6.81 ± 0.08 and 2221 ± 45 mg/L, respectively. Only one out of ten dug wells located in a radius of about a kilometer from Karadiyana dumpsite can be classified as good water for drinking purposes though eight of ten are used for drinking at the moment. All ten dug wells exceeded the WHO recommended nitrate level.

Keywords: Groundwater pollution, Karadiyana open dumpsite, Landfill leachate, Leachate pollution index, Metal pollution index

INTRODUCTION

Municipal landfills are a common feature in many Sri Lankan cities and it has been estimated that there

are more than 260 small and large scale landfills in Sri Lanka (Jayaweera *et al.*, 2019; Koliyabandara *et al.*, 2020). All of the landfills except the ones Dompe and Aruwakkalu can be categorized as unregulated open dumpsites (Jayaweera *et al.*, 2019; Koliyabandara *et al.*, 2020). In addition, most of them have been built without proper environmental impact assessments (EIA) and as a result, dumpsites including Karadiyana, Muthurajawela, Gohagoda, and Ginthota are located very close to sensitive ecological habitats such as major river systems and wetlands in Sri Lanka. According to United States criteria for municipal solid waste (MSW) landfill siting and design, landfills should not be built on wetlands and flood plains, and a proper leachate collection and removal system should be installed to protect groundwater and underlying soil (Letcher & Vallero, 2019). Landfill leachate has been identified as one of the major sources of pollutants to ground and surface waters (Mor *et al.*, 2006). Landfill leachate is the liquid leaching out of landfills due to the infiltration of rainwater through solid waste piles in dumpsites. The leaching liquids are carrying all the water-soluble and suspended fractions of waste and waste degradation by-products. In addition, liquids squeezing out of waste in landfills with a high-water content is also known as leachate. Leachate generation may not be significant in very dry climates (Letcher & Vallero, 2019). Landfills in wet climates and those receiving waste containing a high water content produce a significant amount of leachate (Letcher and Vallero, 2019). The chemical composition

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of leachate consists of a variety of components including particulate and dissolved organic matter, heavy metals, and inorganic compounds, due to the mixed nature of the waste in many landfills (de Godoy Leme & Miguel, 2018).

The risk of pollution of surface water and groundwater sources closer to dumpsites, such as dug and tube wells, rivers, and streams, which are used by humans for drinking or sanitary purposes, is most severe in open dump sites because of the lack of engineered liners and leachate collection systems (El-Salam & Abu-Zuid, 2015). The type and depth of the water table, the direction of groundwater flows, and the concentration of pollutants determine the severity of ground and surface water pollution (Aderemi *et al.*, 2011). Many toxic metals make stable water-soluble complexes with dissolved organic matter, which allows them to transport through the water channels easily. This is a prime issue in Asian countries as most of the landfills do not have liners to prevent contamination of groundwater and underlying soil (Rafizul *et al.*, 2012).

Due to lack of infrastructure and funds, poor landfill and waste management practices, and the negligence of enforcing environment protection laws in Sri Lanka, the country has faced a few landfills related disasters with loss of life and property. The collapse of the Meethotamulla open dumpsite on the 14th April 2017, with a loss of 32 people, was one of them (Jayaweera *et al.*, 2019). The discharge of the organic matter rich Gohagoda landfill leachate into the Mahaweli river, which is the major source of drinking water for the Kandy city, has been reported (Kumarathilaka *et al.*, 2016). In addition, harmful volatile organic compounds (VOCs), including benzene and toluene, have been detected in the Gohagoda landfill leachate (Kumarathilaka *et al.*, 2016). The chemical composition of leachate in Kataragama, Negombo, Matale and Hambantota landfills has been investigated previously and it has been found that many leachate samples contained high amounts of organic matter, nutrients, and heavy metals (Sewwandi *et al.*, 2013). The contamination of surface water bodies and sediments by Karadiyana dumpsite leachate has also been reported (Koliyabandara *et al.*, 2020; Mandakini *et al.*, 2016).

The characterization of landfill leachate is essential to investigate the risk of environmental pollution and to design leachate treatment facilities. Characterization of volatile and semi-volatile compounds in landfill leachate has been carried out specifically by GC-MS analysis. The

volatile and semi-volatile compounds in leachate related to cosmetics, medicine, pharmaceuticals, and plastics has been identified by the GC-MS data (Badoil & Benanou, 2009). In a particular study, GC-MS data revealed that a higher number of phosphorus-based compounds were present in leachate from a ten-year old landfill than in leachate from fresh landfill waste (Badoil & Benanou, 2009). In addition, GC-MS analysis has identified chlorinated aromatic xenobiotic organic matter (XOM), and many XOMs were found in the surface waters around dumpsites, indicating that they could be used as landfill leachate tracers (Banar *et al.*, 2009). Previous studies have shown the presence of XOMs, including benzene, methylbenzoic acids, aliphatic carboxylic acids, hydrocarbons, phenylpropionic acid, methyl phenols, aromatic carboxylic acids, and ethylphenols, in landfill leachate (Saadi *et al.*, 2006; Shouliang *et al.*, 2008).

Molecular fingerprinting using fluorescence excitation emission matrixes (EEM)s have been used in many sample matrixes, such as coloured wastewater, sewage effluents and polluted rivers (Ito *et al.*, 2016; Yamashita & Tanoue, 2003). Wastewater characterization with rapid fluorescence analysis has become a reliable and effective method (Stedmon *et al.*, 2003). Fluorescence has been used to fingerprint leachate in previous studies (Baker & Curry, 2004). It has been found that landfill leachate fluorescence properties are all characterized by intense fluorescence at excitation wavelengths (λ_{ex}) 220 to 230 nm, and emission wavelengths (λ_{em}) 340 to 370 nm, which was suggested to be derived from fluorescent components of the XOM fraction such as naphthalene (the "XOM peak"). A second fluorescence center, at λ_{ex} = 320 to 360 nm, and λ_{em} = 400 to 470 nm, is derived from a higher molecular weight fulvic-like fraction, and a third center at λ_{ex} = 270 to 280 nm and λ_{em} = 340 to 360 nm to tryptophan-like fluorescence.

Development of indexes such as leachate pollution index (LPI), water quality index (WQI), metal pollution index (MPI) and heavy metal pollution index (HPI/HMPI) to assess the pollution potential of landfill leachate provide essential information about the extent of pollution caused by dump sites (Giriappanavar & Patil, 2013; Umar *et al.*, 2010). The leachate pollution index is based on several pollution parameters which express the total leachate contamination potential of a landfill. Values exceeding 7.5 for LPI are an indication of an increased potential for environmental pollution (Umar *et al.*, 2010). Calculation of LPI can be useful in recognizing an appropriate landfill design, in forecasting the effect of leachate on the groundwater quality, identification

of hazard potential of leachate and developing proper mechanisms for the treatment of leachate (Sharma *et al.*, 2008). The water quality index (WQI) is also a useful technique in assessing water quality. Water quality parameters are converted to an overall index with the use of mathematical tools (Logeshkumaran *et al.*, 2015). One of the most commonly used WQI's was developed by the Canadian Council of Ministers of the Environment (CCME). It is known for its ease of use in summarizing a wide array of data (Giriappanavar & Patil, 2013).

It is essential to assess the contamination potential of landfill leachate to mitigate the risks associated with it. The main objective of the current study is to characterize leachate from the Karadiyana open dumpsite for the purpose of determining its potential to pollute water sources in its vicinity. In addition, the extent of ground water pollution of nearby dug wells generally used for drinking, washing, and sanitary purposes has also been assessed to evaluate their suitability for domestic use.

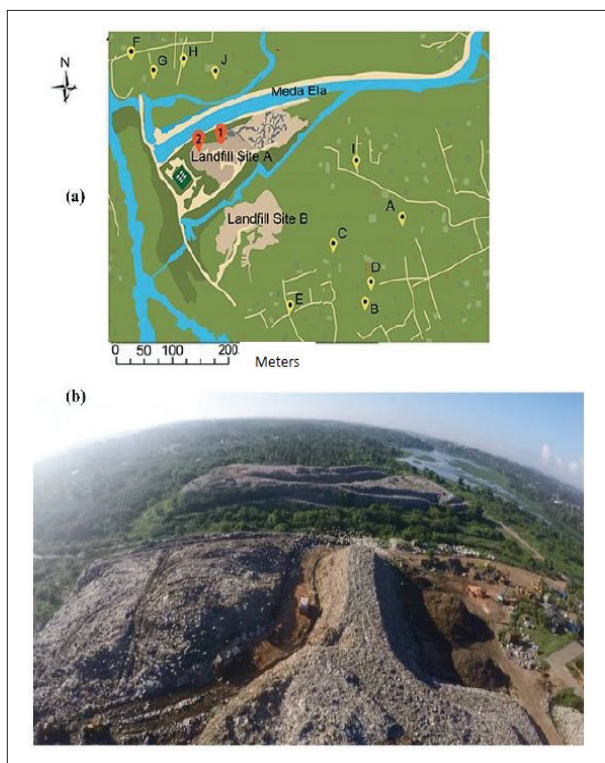


Figure 1: (a) Karadiyana solid waste dumpsite with leachate collection points 1, and 2, and groundwater collection points (dug wells) from A to J. (b) Birds eye view of the Karadiyana Dumpsite.

MATERIALS AND METHODS

Study area

The Karadiyana Waste Management Facility (6°48'58.32"N, 79°54'9.90"E), located in Kesbewa, Western Province of Sri Lanka, has a total area of about 0.10 km² with two waste dumping sites; site A that covers approximately 0.048 km² and site B that covers approximately 0.052 km² (Figure 1). The two waste dumping sites are separated by a canal. Site A was the active site receiving waste from local authorities and other public institutions during the study period (2016-2018). Karadiyana is the final waste disposal site for daily collected mixed and separated waste at a loading rate of approximately 575 T/day. It has been in operation for nearly 20 years as an unregulated open dumpsite receiving mixed waste. Because of its location close to a highly residential area, and to an ecologically sensitive Weras Ganga - Bolgoda Lake wetland system, arrangements are now in progress to convert the open dumpsite site into a semi-controlled landfill site.

Leachate and groundwater sample collection and analysis

Leachate samples were collected from two large leachate pools at locations 1 and 2 from site A as shown in Figure 1, during the period October 2016 to June 2018, in six sampling trips. Site A was the active site during the study period while leachate generation from site B was negligible. Lack of access roads to Site B due to its specific location in marshy land was also a reason to collect leachate only from site A. Groundwater samples were collected from 10 dug wells (~10 m deep) located in a radius of 0.5 to 1 km from the dumpsite and their approximate locations are shown in Figure 1. The exact geographical locations of dug wells are not stated in the manuscript due to an agreement with the well owners. All water and leachate samples were collected into acid washed pre-cleaned polypropylene bottles with zero head space to avoid aeration of the samples. Some water quality parameters were analyzed in the laboratory after transporting them in an ice box at 0 to 5 °C, and other parameters were analyzed in the field as described in the following section. All the water and leachate samples were collected, preserved, and tested according to standard methods (Eaton *et al.*, 2005).

The leachate and water samples were filtered (~0.45µm filter pore size) before analysis. Tests were triplicated to maintain accuracy and precision. Water

quality parameters namely biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia, nitrate, nitrite, and the metals Cu, Fe, Zn, and Mn were determined. The determination of BOD₅ was done by the Winkler method, and the COD was done by the Cr₂O₇²⁻ oxidation method. Nitrate, nitrite, and ammonia analysis were done in the field using a YSI photometer and Palintest reagents. Leachate and surface water samples were digested with a sulphuric - nitric acid mixture prior to measuring total phosphates using YSI Model 9500 photometer and Palintest reagents. The total metal concentrations of copper (Cu), manganese (Mn), zinc (Zn), and iron (Fe) were determined because of their availability in landfill leachates. The leachate, and water samples were digested using high purity nitric acid before metals analysis using a Thermo Scientific iCE 3000 series atomic absorption spectrophotometer in flame and graphite furnace modes. Groundwater samples from dug wells were analyzed for anions using a Metrohm 930 IC flex ion chromatograph. YSI EXO2 water quality SONDE was used to estimate the pH and EC onsite.

Leachate characterization using fluorescence data

Leachate samples were brought to the laboratory and tested within 24 h. Samples were first filtered using Whatman microfiber filter papers previously heated to 450 °C to remove any organic matter. Fluorescence excitation-emission matrixes (EEMs) were produced using a Thermo Scientific luminescence spectrophotometer as described previously (Baker & Lamont-Black, 2001). A scan was carried out with excitation wavelengths from 200 to 370 nm and the emission were recorded from 250 to 500 nm and the samples were diluted when necessary. Absorption correction was not applied to the fluorescence spectra. The excitation and emission data were used to prepare excitation-emission matrixes (EMMs) which are then used to identify the major functional groups of fluorescent compounds in the leachate based on the position of the excitation and emission band peaks.

Leachate characterization using gas chromatography-mass spectrometry (GC-MS)

The volatile and semi-volatile organic fractions of landfill leachate was determined by GC - MS analysis (Agilent 7890A GC coupled to 5975C MS with Triple-Axis Detector) with HP5-MS capillary column (30 m, 0.25 mm, 0.25 µm). First, 200 mL of leachate samples were filtered through a 0.45 µm membrane, and then extracted with 30 mL CH₂Cl₂ (HPLC grade) at pH

values in the order of 7.0, 2.0 and 12.0. During the extraction process, the extract mixture was demulsified by centrifuging at 4000 rpm for 10 min. All the extract was mixed together, dehydrated with anhydrous Na₂SO₄, and then condensed to 1 mL with a rotary evaporator. The oven temperature of the GC was initially set at 65 °C and maintained for 2 min, then programmed to 220 °C at a rate of 9 °C min⁻¹ and maintained for 20 min. The injector was operated in a spitless mode, and the temperature was 300 °C. The MS was run at a voltage of 1050 V, electron ionization with electron energy of 70 eV, and an ion source temperature of 200 °C (Lei & Aoyama, 2010).

Calculation of leachate pollution index (LPI) and water quality index (WQI), metal pollution index (MPI)

The LPI of the Karadiyana dumpsite leachate was calculated with the sum of cumulative pollution ratings of all variables according to the following equation (Kumar & Alappat, 2005).

$$LPI = \sum_{i=1}^n w_i p_i / \sum_{i=1}^n w_i \quad \dots(1)$$

In equation (1), w_i is the weight factor for the i^{th} pollutant variable, p_i is the sub-index score of the i^{th} pollutant variable, and n is the number of known concentrations of leachate contaminant variables. Averaged sub-index curves are used to calculate the sub-index values as stated previously (Kumar & Alappat, 2005). The importance level of each parameter is considered when calculating the weights of individual parameters.

The WQI developed by CCME was used for analyzing ten dug well water samples using equation 2 where three elements known as F1 (scope), F2 (frequency) and F3 (amplitude) are calculated (CCME, 2001). Water quality parameters were given weights according to their importance, and the suitability of water for purposes like drinking, recreation, irrigation, and livestock was assessed accordingly.

$$CCME\ WQI = 100 - \sqrt{(F1^2 + F2^2 + F3^2)} / 1.732 \quad \dots(2)$$

In the equation F1 represents the number of variables that do not meet the water quality standards as a percentage. F2 represents the number of individual tests that do not meet the water quality standards as a percentage. F3 states the amount by which failed test values do not meet their guideline values.

The metal pollution index (MPI) was used to measure the overall metal content at the various sampling sites by using equation 3 (Usero *et al.*, 2005).

$$MPI = \frac{\sum_{i=1}^n w_i Q_i}{\sum_{i=1}^n w_i} \quad \dots(3)$$

Where w_i is the weightage of each parameter which is taken by inversely proportionate value of its standard value. Q_i is the sub index of i^{th} parameter. It can be calculated by the equation below.

$$Q_i = \frac{(M_i(-)I_i)}{(S_i(-)I_i)} \quad \dots(4)$$

Here M_i is the mean concentration value of a parameter, S_i is the standard permissible value and I_i is the highest desirable value of each parameter.

RESULTS AND DISCUSSION

Characterization of Karadiyana landfill leachate

The physicochemical characteristics of Karadiyana leachate were determined on two large leachate pools that were present during the entire study period as some of the other leachate pools were dried out in the dry season. In addition, some leachate pools were unreachable due to their location within the dumpsite and lack of access roads. The two sampled leachate pools had formed by merging several small leachate-flows in a depression of about 2 m in diameter with a depth of about 1 m. These pools were very close to the Meda-Ela canal, and it was observed that the pools overflow directly into the canal. The average values of leachate characteristics,

Table 1: The average values of the physicochemical characteristics of the Karadiyana open dump leachate with standards of tolerance limits for the discharge of effluent to inland surface waters by the Central Environmental Authority (CEA) of Sri Lanka (CEA, 2008)

Date	pH	EC $\mu\text{S}/\text{cm}$	NO_3^- mg/L	NH_3 mg/L	Total PO_4^{3-} mg/L	Cu mg/L	Fe mg/L	Zn mg/L	Mn mg/L	COD mg/L	BOD_5 mg/L	BOD/COD
Location 01												
10/2016	6.76	7,417.0	167.8	505.0	42.0	0.69	10.80	0.23	0.40	1,933	931	0.48
01/2017	6.80	6,598.0	153.2	451.9	31.0	0.44	9.66	0.35	0.38	1,800	723	0.40
06/2017	6.91	4,800.0	147.4	412.0	28.0	0.69	10.80	0.48	0.40	2,705	1,048	0.39
10/2017	6.70	4,300.0	145.9	527.2	31.0	0.40	8.70	1.20	0.41	1,908	938	0.49
02/2018	6.91	3,600.0	104.6	416.4	38.0	0.41	11.20	1.65	0.61	2,682	1,107	0.41
06/2018	6.78	1,100.0	21.9	376.6	33.0	0.70	10.50	0.30	0.58	2,300	968	0.42
Min.	6.70	1,100.0	21.9	376.6	28.0	0.40	8.70	0.23	0.38	1,800	723	0.39
Max	6.91	7,417.0	167.8	527.2	42.0	0.70	11.20	1.65	0.61	2,705	1,107	0.49
Avg.	6.81	4,636.0	123.5	448.2	33.8	0.55	10.28	0.70	0.46	2,221	953	0.43
Stdev.	0.08	2,249.4	54.0	58.2	5.12	0.15	0.93	0.58	0.10	403	132	0.04
Location 02												
10/2016	7.83	6,800.0	145.9	580.3	84.00	0.13	11.20	1.24	0.60	1,406	820	0.58
01/2017	7.50	5,600.0	155.6	509.5	72.00	0.01	7.50	2.10	0.47	1,380	648	0.47
06/2017	6.89	4,700.0	167.8	513.9	60.00	0.13	11.20	1.24	0.32	2,800	1,220	0.44
10/2017	6.70	3,800.0	145.9	434.1	45.00	0.07	10.20	2.20	0.38	2,400	1,280	0.53
02/2018	6.89	3,210.0	68.1	500.6	18.00	0.04	9.30	1.70	0.42	2,933	1,365	0.47
06/2018	6.80	2,900.0	20.7	487.3	10.00	0.11	10.80	1.30	0.45	2,703	1,630	0.60
Min.	6.70	2,900.0	20.7	434.1	10.00	0.01	7.50	1.24	0.32	1,380	648	0.44
Max.	7.83	6,800.0	167.8	580.3	84.00	0.13	11.20	2.20	0.60	2,933	1,630	0.60
Avg.	7.10	4,501.7	117.3	504.3	48.17	0.08	10.03	1.63	0.44	2,270	1,160	0.52
Stdev.	0.45	1,500.3	59.0	47.2	29.56	0.05	1.43	0.44	0.09	702	363	0.07
CEA	6.5-8.5	N/A	50	N/A	5	3	3	2	N/A	250	30	N/A

N/A Not available

Biochemical oxygen demand (BOD), chemical oxygen demand (COD)

determined using leachates collected during field trips between October 2016 and June 2018, are shown in Table 1.

According to the results, it is evident that the raw leachate does not meet the tolerance limits especially for ammonia, phosphate, BOD and COD levels for the discharge of effluent to inland surface waters specified by the Central Environmental Authority of Sri Lanka. The raw leachate from Karadiyana dump site must not directly flow into any surface or groundwater without treatment, as the contamination of Meda-Ela canal would lead to detrimental effects on the environment as a whole. The experimental data collected in this study shows that the pH of Karadiyana leachate ranged from 6.7 to 7.8, which is suitable for methanogenic bacteria. Literature states that generally, leachate shows pH values between 4.5 to 9.0 and the pH of leachate increases with the decrease of concentration of partially ionized free volatile fatty acids (Tatsi & Zouboulis, 2002). The pH of leachate greater than 7.5 marks the landfill as old while pH lower than 6.5 states that it has newer leachate (Robinson, 2007). The pH values of the landfill leachate increase with the aging of the landfill due to the biological decomposition of organic nitrogen into ammonium-N (Chen, 1996). Leachate samples with a slightly high pH ranging between 7.0 to 8.0 indicate the short acidic phase and early methanogenic phase (Tränkler *et al.*, 2005). On

the other hand, landfill leachate in Malaysia has shown an average value of pH around 6.7, which indicates that the leachate is recent, and the waste degradation is at the final stage of its acidic phase (Bahaa-Eldin *et al.*, 2008).

Nitrate, ammonia, and total phosphate in leachate varied in the range of 20.7 to 167.8, 376.0 to 580.0 and 10.0 to 84.0 mg/L respectively during the study period. Both new and old leachate is characterized by ammonia nitrogen, and hydrolysis and fermentation of the nitrogenous fraction of biodegradable waste cause older leachate to have a significant amount of ammonia nitrogen (Kulikowska & Klimiuk, 2008). Studies carried out in a Nigerian open dumpsite has recorded an average nitrate concentration of 55.82 ± 12.31 mg/L (Ibezute & Erhunmwunse, 2018). In comparison to several studies carried out worldwide, Karadiyana leachate shows values into the upper ranges exceeding 100 mg/L. Ammonia levels present in open dumpsite leachate recorded in other studies have ranged from 500 to 1500 mg/L (Tatsi & Zouboulis, 2002). In this study the average ammonia concentration was recorded as 448.2 mg/L. A major open dumpsite in Sri Lanka, Gohagoda has recorded values ranging between 6.0 to 4095.0 mg/L for ammonia nitrogen (Wijesekara *et al.*, 2014). Old leachate was determined to have nitrate values below 100 mg/L and ammonia is considered as a principal pollutant in old leachate because of the deamination of amino acids

Table 2: Pearson correlation matrix of parameters of leachate with rainfall variation

Location 1						
	Rainfall (mm)	NO ₃ ⁻ (mg/L)	NH ₃ mg/L	PO ₄ ³⁻ (mg/L)	COD (mg/L)	BOD (mg/L)
Rainfall (mm)	1.00					
NO ₃ ⁻ (mg/L)	0.32	1.00				
NH ₃ mg/L	0.80	0.73	1.00			
PO ₄ ³⁻ (mg/L)	0.06	0.06	0.24	1.00		
COD (mg/L)	-0.52	-0.34	-0.69	-0.12	1.00	
BOD (mg/L)	-0.08	-0.29	-0.33	0.17	0.85	1.00
Location 2						
Rainfall (mm)	1.00					
NO ₃ ⁻ (mg/L)	0.33	1.00				
NH ₃ (mg/L)	-0.26	0.19	1.00			
PO ₄ ³⁻ (mg/L)	0.26	0.87	0.57	1.00		
COD (mg/L)	-0.19	-0.50	-0.51	-0.80	1.00	
BOD (mg/L)	-0.01	-0.73	-0.53	-0.90	0.89	1.00

during destruction of original organic compounds. The phosphate levels present in leachate samples are comparable to those in studies carried out under the same environmental conditions and similar age of generation (Robinson, 2007; Wijesekara *et al.*, 2014).

According to the literature, a low BOD/COD (<0.5) ratio results due to the presence of higher amounts of humic and fulvic like compounds and low concentrations of volatile fatty acids (Kjeldsen *et al.*, 2002). A BOD/COD ratio greater than 0.5 suggests that the leachate originates from fresh (new) organic waste in a landfill. If the ratio decreases, approaching 0.1, studies have found out that it originates from an old and stable landfill (Kjeldsen *et al.*, 2002). The present study reveals that the leachate has BOD/COD values in the range of 0.39 to 0.60. It indicates that Karadiyana leachate is in its intermediate phase. As the site receives fresh MSW daily, generation of new leachate is possible. Showing values lower than 0.5, indicates that the Karadiyana landfill leachate has a relatively higher amount of humic and fulvic like compounds. The decay of organic matter into amino acids can affect the values of BOD, COD, and the ratio of BOD/COD. Values recorded for BOD/COD ratio for Sri Lankan dumpsites in Gohagoda, Matale and Kataragama are 0.08, 0.02 and 0.04 respectively, highlighting the presence of mature landfill leachate (Sewwandi *et al.*, 2013; Wijesekara *et al.*, 2014).

The temporal distribution of leachate varies along with rainfall as it facilitates mobility or dilution of

pollutants (Tränkler *et al.*, 2005). Correlation analysis for the parameters of leachate along with the rainfall variation is shown in Table 2. Rainfall shows strong positive correlation (0.8) with NH_3 in location 1. Nitrate and rainfall show positive correlation in both locations (location 1- 0.32, location 2- 0.33). It was also observed that the correlation coefficients between certain parameters are significantly different in the two locations. These include correlations between nitrate and phosphate, phosphate and BOD, and ammonia and rainfall. The exact reason for these differences is difficult to comprehend and it could be due many factors. It appears that the two leachate pools have slightly different chemical compositions. Leachate in Location 1 has more nitrate, and Cu than Location 2. On the other hand, Location 2 has more Zn, biodegradable carbon (ex-BOD) and phosphate than Location 1. The BOD/COD ratios of the locations are also different from each other. It is possible that these differences play an important role in the overall chemical and biological degradation processes taking place in leachate. As a result, correlation coefficients between certain parameters could be significantly different in the two locations.

Leachate pollution index

The sub-index values were calculated from averaged sub-index curves reported previously (Kumar & Alappat, 2005). An LPI value higher than 7.5 specifies that leachate can cause harm for both the environment and human health (Esakku *et al.*, 2007). The leachate pollution index

Table 3: Leachate pollution index (LPI) calculation for Karadiyana leachate

Parameter	Pollutant concentration	Sub-index value p_i	$W_i = \text{weight/total weight}$	Cumulative pollution rating ($\sum w p_i$)
pH	7.10	5	0.03	0.17
Ammonia (mg/L)	504.3	45	0.30	13.50
Nitrate (ppm)	117.3	5	0.03	0.17
Cu (mg/L)	0.08	5	0.03	0.14
Fe (mg/L)	10.03	5	0.03	0.14
Zn (mg/L)	1.63	5	0.03	0.14
Mn (mg/L)	0.44	5	0.03	0.14
COD (mg/L)	2,270.33	45	0.30	13.50
BOD (mg/L)	1,160.50	30	0.20	6.00
Total		150	1	34.00

of the Karadiyana open dumpsite was calculated as 34.00 (Table 3). Elevated levels of ammonia and COD make a major contribution to the cumulative pollution rating, indicating the effect of inorganic and organic pollution in the Karadiyana dumpsite. Open dumps located in similar environmental conditions (wet zone) in Sri Lanka have recorded LPI value of 31.31 for Bandaragama and 42.50 for Kolonnawa (Sewwandi *et al.*, 2013).

Characterization of dissolved organic matter (DOM) in leachate using fluorescence and GC-MS techniques

DOM in Karadiyana leachate was identified using fluorescence spectroscopic methods. Four major groups were identified, namely, tryptophan and tyrosine like protein fractions, and fulvic and humic fractions shown in Figure 2. Similar characterization has been carried out in previous research (Koliyabandara *et al.*, 2019). The presence of volatile fatty acids is identical in new leachate and in intermediate-age leachate. These are aliphatic mono-carboxylic acids with 2 to 6 or even 7 carbon atoms. These acids are generated due to the presence of massive loads of biodegradable waste (Stegmann *et al.*, 2005). Anaerobic fermentation is the process by which such acids are generated.

The GC-MS studies of Karadiyana leachate provide evidence for the presence of dodecyl acrylate, known to be an environmental hazard, phenol, 4-hydroxypyridine-

1-oxide, phthalic acid, nonadecane, eicosane, and hexadecane. Previous studies have shown the presence of benzene, methylbenzoic acids, aliphatic carboxylic acids, hydrocarbons, aliphatic compounds, phenylpropionic acid, methylphenols, aromatic carboxylic acids and ethylphenols in landfill leachate (He *et al.*, 2006; Saadi *et al.*, 2006). The concentrated leachates have shown the presence of ethylbenzene, chlorobenzene, and the esters of phthalic acid including dibutyl phthalate, dimethyl phthalate, and di-n-octyl phthalate. In all leachates, aliphatic carboxylic acids, and aromatic carboxylic acids such as benzoic acid, methylbenzoic acid, phenylacetic acid, and phenylpropionic acid have been detected. These acids are predominant components of the leachates (Zhang *et al.*, 2013). Researchers have identified toluene and ethyl methylbenzene in addition to esters of fatty acids, and aliphatic and aromatic alcohols (Trzcinski & Stuckey, 2010). The presence of toluene, trichlorethylene, benzene, toluene, and xylenes in leachate have also been identified in previous studies (DeWalle & Chian, 1981).

Assessment of the effects of leachate on groundwater quality

The average values of water quality parameters of dug wells located around the site are presented in Table 4 and Table 5. Most of the residents around the site still use dug-well water for washing and drinking purposes due to ease of access. Most of the water quality parameters

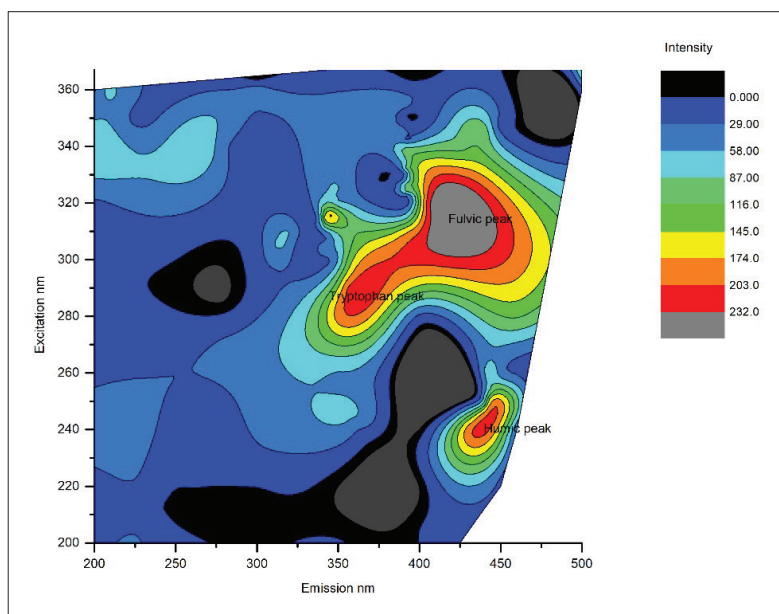


Figure 2: Fluorescence excitation-emission matrix for Karadiyana leachate DOMs.

of dug well water showed values below WHO drinking water standards (WHO, 2011) other than for nitrate and ammonia. Serious health issues can occur if nitrate levels in drinking water exceed 50 mg L⁻¹. All the dug-well water samples showed nitrate values above this limit, which indicates the possibility of mixing of leachate from the Karadiyana dump site. Unusually high nitrate levels have been observed in dug well E which is situated closer to the dump site. Contamination from leachate plumes and/or mixing with septic waste might have caused such higher concentrations. Dissolved nitrogen, which is present in the form of nitrates, is known to be one of the most common contaminants present in groundwater (Chaudhary *et al.*, 2010). Nitrate becomes hazardous when it is reduced to nitrite in the intestine. Hemoglobin is converted to methemoglobin

by nitrite which blocks oxygen transfer. The resulting condition is known as methemoglobinemia, which is even called blue baby syndrome (Kross, 2002). Elevated ammonia levels could be toxic in the environment and ammonification causes the production of ammonia and ammonium compounds by the degradation of nitrogen. It is known as an endogenously produced toxin (Wang *et al.*, 2007). Ammonia can cause a diverse range of diseases, including metabolic disorders, neurological malfunctions, coma, and even death (Ye *et al.*, 1997). Dug wells A, B, C, D, E, I and F, G, H, J can be considered as two separate groups according to their specific location. Considering ammonia and nitrate values of these samples the p value suggests that at 0.05 level there is a significant difference between these sample groups (NO_3^- - 5.51×10^{-6} , NH_3 - 9.36×10^{-5}).

Table 4: Water quality of dug wells around the dump site (n = 50, Data is shown as Average $\pm$ Stdev)

Location	Use for drinking	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	DO (mg/L)	BOD (mg/L)	NO_3^- (mg/L)	NH_3 (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	Br ⁻ (mg/L)
A	✓	7.51 ± 0.08	434.6 ± 5.4	258.4 ± 5.9	3.66 ± 0.08	24.7 ± 1.3	118.29 ± 5.93	0.43 ± 0.04	0.05 ± 0.01	38.25 ± 0.85	0.10 ± 0.01
B	✓	6.42 ± 0.24	254.8 ± 2.3	152.8 ± 1.9	4.85 ± 0.15	12.2 ± 0.8	34.78 ± 1.46	0.74 ± 0.07	0.03 ± 0.01	25.35 ± 0.79	0.05 ± 0.00
C	✓	6.65 ± 0.11	135.8 ± 2.1	85.0 ± 2.6	5.03 ± 0.19	9.8 ± 1.1	31.66 ± 1.16	0.87 ± 0.03	0.07 ± 0.01	27.37 ± 0.53	0.13 ± 0.04
D	✓	7.51 ± 0.17	529.2 ± 6.2	316.2 ± 1.9	5.15 ± 0.15	8.5 ± 0.4	63.42 ± 0.97	0.64 ± 0.04	0.01 ± 0.002	28.14 ± 0.26	0.31 ± 0.03
E	X	8.70 ± 0.04	648.7 ± 2.4	402.0 ± 5.4	4.35 ± 0.17	12.6 ± 0.4	406.62 ± 1.71	2.04 ± 0.04	0.01 ± 0.001	27.66 ± 0.15	0.34 ± 0.02
F	✓	6.74 ± 0.02	117.5 ± 1.0	71.8 ± 1.3	4.77 ± 0.13	63.8 ± 2.5	20.37 ± 1.39	0.14 ± 0.01	0.08 ± 0.002	29.28 ± 0.24	0.15 ± 0.04
G	X	6.88 ± 0.04	197.1 ± 1.0	118.0 ± 0.9	5.40 ± 0.05	83.6 ± 0.4	46.10 ± 0.66	0.27 ± 0.04	0.36 ± 0.33	10.78 ± 0.08	0.18 ± 0.01
H	✓	6.40 ± 0.05	261.6 ± 1.6	161.0 ± 4.5	4.68 ± 0.09	31.4 ± 1.3	73.64 ± 0.73	0.70 ± 0.04	0.05 ± 0.01	44.05 ± 1.00	0.12 ± 0.01
I	✓	6.37 ± 0.11	175.7 ± 0.7	105.1 ± 0.9	4.80 ± 0.04	22.8 ± 0.6	54.58 ± 1.45	0.35 ± 0.02	0.05 ± 0.01	83.04 ± 0.53	0.21 ± 0.01
J	✓	6.43 ± 0.04	260.6 ± 1.7	160.0 ± 4.2	4.67 ± 0.05	9.3 ± 0.2	323.06 ± 1.07	0.89 ± 0.04	0.04 ± 0.01	34.23 ± 0.80	0.07 ± 0.01
WHO 2011		6.5 - 8.5	N/A	500	N/A	N/A	50.0	N/A	1.5	250	1

The concentrations of selected heavy metals in dug wells are shown in Table 4. The presence of the metals, Fe, Zn, Cd, Cr, and Pb in the water samples exceeded the permissible levels set by WHO for drinking water (WHO, 2011). Elevated Cr levels in dug wells D and G might have been caused by vehicle tinkering and painting workshops observed in the vicinity of these wells. Only Mn and Cu showed values below the permissible maximum. Studies carried out for the evaluation of groundwater in Kelantan, Malaysia closer to an open dumping area has recorded values in the range of 0.80 to 47.40 mg/L for Fe, 0.20 to 3.0 mg/L for Cu, 1.10 to 109.70 mg/L for Zn, 0.10 to 1.20 mg/L for Cr and 0.20 to 40.00 mg/L for Mn (Ab Razak *et al.*, 2015).

Metal pollution index

The metal pollution index (MPI) is a method for ranking the quality of water. The index is the single resultant effect of every heavy metal on water quality and is designed to determine the water quality's effect on human health. If the index is greater than 100, the water is deemed hazardous to human health (Zhang *et al.*, 2009). At a

value of 100, the threshold of human health relative to water pollution has been reached. If the index is below 100, there is no significant heavy metal pollution, and there is much less of a cause of concern for consumers of the water. Well water in location E has an MPI of 120.34 and could be categorized as polluted water according to the MPI. It should be noted that, even though the MPI values in other locations were less than 100, the water could not be categorized as less polluted water due to the presence of toxic heavy metals Cr, Cd and Pb at elevated concentrations.

Water quality index

The water quality index according to CCME parameters, which are considered to be relevant to potability and health, should be prioritized when assessing drinking water quality. Potability related parameters are given as pH, EC, and chloride while health-related parameters are indicated as fluoride, nitrate, Fe, Mn, Zn, Cd, Cr, Cu, and Ni. Table 6 lists the CCME water quality index classification for dug wells around the site.

Table 5: Average metal concentrations of dug well water (n=100)

Location	Cu (mg/L)	Zn (mg/L)	Mn (mg/L)	Cd (mg/L)	Cr (mg/L)	Pb (mg/L)
A	0.051 ± 0.003	0.356 ± 0.004	0.079 ± 0.003	0.078 ± 0.005	0.662 ± 0.011	0.266 ± 0.005
B	0.030 ± 0.002	0.201 ± 0.013	0.049 ± 0.002	0.049 ± 0.003	0.419 ± 0.003	0.146 ± 0.003
C	0.109 ± 0.011	0.118 ± 0.003	0.030 ± 0.002	0.059 ± 0.003	0.051 ± 0.002	1.772 ± 0.055
D	0.064 ± 0.073	0.183 ± 0.019	0.037 ± 0.009	0.036 ± 0.013	31.70 ± 8.512	0.132 ± 0.011
E	0.329 ± 0.054	0.639 ± 0.087	0.350 ± 0.088	0.207 ± 0.014	0.104 ± 0.012	2.117 ± 0.050
F	0.114 ± 0.056	0.714 ± 0.666	0.027 ± 0.005	0.018 ± 0.006	0.017 ± 0.005	1.073 ± 0.095
G	0.239 ± 0.002	0.170 ± 0.001	0.030 ± 0.001	0.012 ± 0.001	42.30 ± 0.092	6.750 ± 0.115
H	0.218 ± 0.099	0.797 ± 0.451	0.218 ± 0.083	0.136 ± 0.043	0.043 ± 0.012	2.488 ± 0.156
I	0.094 ± 0.018	0.245 ± 0.055	0.090 ± 0.001	0.056 ± 0.005	0.030 ± 0.000	1.655 ± 0.020
J	0.123 ± 0.019	0.185 ± 0.029	0.095 ± 0.014	0.072 ± 0.004	0.037 ± 0.005	2.082 ± 0.162
WHO 2011	2.00	0.05	0.40	0.003	0.05	0.010

One out of ten dug wells can be classified as having good water under the category of drinking water, while five out of ten dug wells fall into the marginal water category. Regardless of the information obtained from water quality and metal pollution indexes, special care needs to be taken before using well water for domestic use because of the presence of toxic chemical compounds in the water.

Tracing landfill leachate

The use of tracers for the identification of pollution routes have been tested in studies carried out worldwide specially for the detection of groundwater contamination and surface water monitoring activities (Baker & Lamont-Black, 2001). Especially, in tracing leachate pollution occurring from open dumpsites, constituents

such as ammonia, bromide, and fluoride have been used in achieving the target, and ammonia may also be deemed a beneficial tracer of landfill leachate in surface waters, with average concentrations of leachate

mentioned (50 – 2,200 mg/L) (Christensen *et al.*, 2001). Fluorescence tracing of leachate has shown reliable results and it is a time saving and cost effective method (Baker & Lamont-Black, 2001). Looking at the

Table 6: WQI and classification of water quality of dug wells around the Karadiyana site

Location	Usage - drinking	Overall	Drinking	Aquatic	Recreation	Irrigation	Livestock
A	√	63 Marginal	50 Marginal	100 Excellent	100 Excellent	100 Excellent	57 Marginal
B	√	76 Fair	67 Fair	79 Fair	100 Excellent	100 Excellent	71 Fair
C	√	86 Good	78 Fair	100 Excellent	100 Excellent	100 Excellent	72 Fair
D	√	68 Fair	56 Marginal	100 Excellent	100 Excellent	100 Excellent	65 Fair
E	x	40 Fair	29 Poor	100 Excellent	100 Excellent	100 Excellent	44 Poor
F	√	82 Good	82 Good	100 Excellent	100 Excellent	100 Excellent	100 Excellent
G	x	84 Good	73 Fair	100 Excellent	100 Excellent	100 Excellent	69 Fair
H	√	68 Fair	55 Marginal	73 Fair	100 Excellent	100 Excellent	63 Marginal
I	√	72 Fair	60 Marginal	75 Fair	100 Excellent	100 Excellent	67 Fair
J	√	70 Fair	57 Marginal	75 Fair	100 Excellent	100 Excellent	63 Marginal

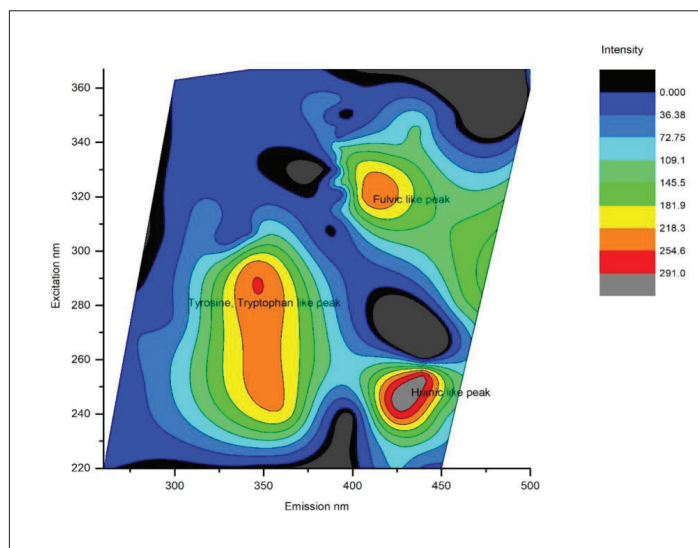


Figure 3: Fluorescence excitation-emission matrix for Karadiyana leachate DOMs from Location E.

fluorescence peaks present in dug well water samples; λ_{em} 320-340 nm and λ_{ex} 270-280 nm, it shows a large amount of unsaturated (aromatic) carbon bonding per organic carbon as well as much more complex organic structures, and these are assigned to the omnipresent tyrosine and tryptophan substances. Fluorescence studies help to identify and assume the possible contamination by leachate. Dug well E, which was recorded as having poor water quality, was characterized by the presence of humic fractions (240/440 nm), fulvic nature (310 – 340/420 – 440 nm), and tryptophan and tyrosine amino acids (240 – 300/350), as shown in Figure 3.

CONCLUSIONS

In this study, characterization of leachate generated by the Karadiyana open dumpsite and the contamination of water sources in the vicinity of the dumpsite were assessed. A leachate pollution index of 34.00 in the Karadiyana dumpsite suggests that the leachate is highly polluted, and appropriate treatment and a pollution mitigation process is essential before discharging into the neighboring water sources and environment. The fluorescence spectra of leachate showed the occurrence of tryptophan, tyrosine like substances, and humic substances. These compounds are present in intermediate (5 to 10 years) and old/stabilized (more than 10 years) leachate. A BOD/COD ratio of leachate in present study varies between 0.39 and 0.49 which categorizes leachate as intermediate in age, where biodegradability is medium according to the classification, further proven by an average pH of 6.81 ± 0.08 and an average COD of 2221 ± 45 . The MPI of dug wells showed that one out ten was categorized into the polluted category. The surface and dug well samples around the dumpsite were generally neutral, showing pH values in the range of 6.5 to 8.5. Some of the dug wells, which are used by residents for drinking purposes, have nitrate levels above the WHO recommended levels, which could lead to detrimental health effects. Location-specific water quality parameter variation is present, and the use of mitigation methods can be carried out on the flow direction of leachate. Based on the CCME-WQI classification, dug well water is not the best option to be used for drinking purposes because only one out of ten dug wells was classified as producing good water.

Data availability

Supplementary data is available upon request from the corresponding author.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgment

This research project was funded by the University of Sri Jayewardenepura under the research grant ASP/01/RE/SCI/2018/23

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