RESEARCH ARTICLE



A long-term comparative assessment of human health risk to leachate-contaminated groundwater from heavy metal with different liner systems

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Abstract The handling and management of municipal solid waste (MSW) are major challenges for solid waste management in developing countries. Open dumping is still the most common waste disposal method in India. However, landfilling also causes various environmental, social, and human health impacts. The generation of heavily polluted leachate is a major concern to public health. Engineered barrier systems (EBSs) are commonly used to restrict potentially harmful wastes by preventing the leachate percolation to groundwater and overflow to surface water bodies. The EBSs are made of natural (e.g., soil, clay) and/or synthetic materials such as polymeric materials (e.g., geomembranes, geosynthetic clay liners) by arranging them in layers. Various studies have estimated the human health risk from leachate-contaminated groundwater. However, no studies have been reported to compare the human health risks, particularly due to the leachate contamination with different liner systems. The present study endeavors to quantify the human health risk to contamination from MSW

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landfill leachate using multiple simulations for various EBSs. To quantify the variation in health risks to groundwater consumption to the child and adult populations, the Turbhe landfill of Navi Mumbai in India has been selected. The leachate and groundwater samples were collected continuously throughout January–September in 2015 from the landfill site, and heavy metal concentrations were analyzed using an inductively coupled plasma system. The LandSim 2.5 Model, a landfill simulator, was used to simulate the landfill activities for various time slices, and non-carcinogenic human health risk was determined for selected heavy metals. Further, the uncertainties associated with multiple input parameters in the health risk model were quantified under a Monte Carlo simulation framework.

Keywords Heavy metal · Human health risk · LandSim · Liner systems · Monte Carlo · Mumbai · Turbhe

Introduction

The leachate from municipal solid waste (MSW) landfill sites contains a broad mixture of chemical pollutants that can cause potential risks to surface and groundwater bodies (Christensen et al. 2001). The disposal of MSW to landfill sites is the most common waste disposal method in developing countries such as India (Rathod et al. 2013; Mishra et al. 2016a). However, because of the improper management of landfills, high leachate leakage can have adverse impacts on soils, plants, groundwater, aquatic organisms, and, subsequently, human health (Mishra et al. 2016b; Talalaj and Biedka 2016). To prevent soil, ground, and surface water contamination, the use of an engineered barrier system (EBS) in modern landfill sites is a growing concern in most of the developing countries. Landfilling technology has undergone significant developments in the last several decades and evolved from uncontrolled city dumps to highly engineered structures designed to protect the environment. Despite these advancements, it has been reported worldwide that even sanitary landfill sites, which are commonly present in urban areas and used to dispose of waste in a scientific manner, have the potential to pollute groundwater and surface water, which poses risks to human health (Slack et al. 2005).

Landfill liners are constructed to create a barrier between the solid waste and the surrounding environment. The primary purpose of the liner system is to isolate the leachate contaminants from the environment and to protect the soil, surface, and groundwater contamination (Hughes et al. 2007). However, the selection of an appropriate liner for a landfill site must be designed based on the site location, geology, depth of the groundwater table, solid waste type, and regional meteorological data, which include precipitation, temperature, and other weather parameters. Various studies have demonstrated the leachate transport to groundwater (Jagloo 2002; Slack et al. 2007; Palmeri et al. 2012; Plimmer et al. 1999). However, very few studies have evaluated the performance of the various liner systems in landfill sites.

To protect the human health and environment, risk assessment (RA) has become a dominant public policy tool for decision making (Butt et al. 2014). The goal of RA is "to estimate the severity and likelihood of adverse human health impacts from exposure to a substance that, can cause harm to public health" (Kentel and Aral 2004). RA procedure has been applied to estimate the adverse impacts from exposure to contaminated water via multiple exposure pathways and routes such as ingestion (drinking), inhalation (breathing volatilized contaminants during showering), and dermal contact (skin contact with contaminated water). The RA procedure for investigating the long-term risk of leachate-contaminated groundwater can render an affordable technique for local administrations/municipalities particularly when economic resources are inadequate (Palmeri et al. 2012; Mishra et al. 2016b).

Landfill leachate transport modeling typically involves two steps: first, the leachate generation and its leakage through the landfill liners and second, the transport and migration of the contaminants to an aquifer or compliance point. Numerous numerical models have been developed to simulate landfill leachate transport in the subsurface. For the present study, a comprehensive literature review of leachate transport modeling was performed and three computer models identified. The three models are the LandSim (http://www.landsim.co.uk/), Pollute (http://www.gemsoft.us/Pollute.htm), and IWEM (Industrial Waste Evaluation Model) (https://www.epa.gov/ smm/industrial-waste-management-evaluation-modelversion-31). The LandSim, Pollute, and IWEM are the only computer models found to be specifically designed to simulate contaminant transport in groundwater. The LandSim (Landfill Performance Simulation) model, developed by Golder Associates, is purely for landfill simulation and broadly used to simulate landfill activities within the waste industry as a decision support tool. This model uses the Monte Carlo simulation (MCS) technique and probabilistically estimates the probable concentrations of pollutants at different levels that can reach on the ground over a period. However, the estimates become less accurate with increasing distance from the landfill to the receptor/monitoring point (Butt and Oduyemi 2003; Butt et al. 2008, 2009). For the effective environmental management of human health risks due to landfill leachate contamination, a holistic RA approach is required that integrates the leachate transport with health risk modeling. To keep the objective of quantitatively estimating the uncertainty of the human health risks to different EBSs, the LandSim 2.5 simulation model was selected in the present study to perform a holistic RA.

Solid waste management (SWM), which includes the collection, transportation, processing, and disposal, is the responsibility of urban local bodies (ULBs) in India. However, the service provided by the ULBs has become inefficient and inadequate because the systems applied are unscientific, outdated, and ineffective, and the population coverage is low due to inadequate provisions in the governing municipal laws (Asnani 2006). In India, the total MSW generated by urban cities in 2011 was 188,500 tons per day, which is a 50% increase since 2001. Most of the cities do not have sanitary landfills, which include major generators such as greater Mumbai, Delhi, and Kanpur (FICCI 2009). The majority of the MSW (more than 91%) collected formally is landfilled on open lands and dumped (Kumar et al. 2009). The MSW (Management and Handling) Rules for 2000 suggest the use of a composite liner at municipal landfill sites in India. Additionally, a 15-year postclosure monitoring (management control) is considered sufficient for preventing landfill impacts in future. However, landfilling is site specific, which is an aspect that involves multiple uncertainties. Therefore, the proposed guidelines by the Ministry of Environment and Forests (MoEF), India, must be reviewed and updated further per scientific study. The present study is an effort to quantify the uncertainty in non-carcinogenic human health risks due to various EBSs for multiple population groups using 10,000 MCSs on the Turbhe landfill in Navi Mumbai, India. This study is the first effort to quantify human health risks due to leachatecontaminated groundwater with different EBSs. The next section describes the study area, which is the Turbhe landfill site in Navi Mumbai, India. The third section explains the sampling and storage method, presents a detailed description of the various liner systems, and presents a comprehensive literature review of the LandSim model followed by a discussion on human health risk assessment (HHRA) and its associated uncertainty. The leachate pollution index (LPI) was estimated for the Turbhe landfill leachate and is provided in the "Results and discussion" section. This section also reports on the leachate leakage through the EBS, the contaminant time history, and quantification of uncertainty in the human health risks. The final, concluding section summarizes the study and identifies the future research scope.

Study area

To quantify the adverse health impacts due to MSW landfill leachate contamination to groundwater resources for different EBSs, the Turbhe landfill site, Navi Mumbai, India, was selected (Fig. 1). Turbhe is a sanitary landfill site with a single liner system and located on the west coast of Maharashtra under the jurisdiction of Navi Mumbai municipal corporation (NMMC). Navi Mumbai is located between 19°5′ N and 19°15′ N latitude and 72°55′ E and 73°5′ E longitude. The geological formations of the study area consist of dark-colored volcanic lava flows, basaltic in composition, and are intruded by a large number of dykes (NMMC 2010). The climate of Navi Mumbai is tropical wet type with average temperature varying from 12 to 43 °C and the

maximum of rainfall (approximately 90%) is experienced during June to September (NMMC 2013). Around 650 metric tons of waste is generated from the residential, commercial, and industrial areas comprising mainly of biodegradable waste. The primary sources of waste are from residential areas, agricultural produce market committee, and Maharashtra industrial development corporation. The composition of MSW in NMMC has been shown in Fig. 2. The waste consists of biodegradable/organic waste (57%) mainly collected from the households and commercial areas and having much larger organic content compared to global solid waste composition (Hoornweg and Bhada-Tata 2012). Paper waste contributes 11% of the total waste in NMMC. The average per capita waste generation is 0.26 to 0.61 g/day (Chourey et al. 2014). An extensive study for analyzing Turbhe landfill leachate has been performed by Mishra et al. (2016a), and a generic framework for assessment and characterization of MSW landfill leachate has been proposed. Further, an integrated approach in the form of a framework has been proposed by Mishra et al. (2016b) to quantify the uncertainty that is intrinsic to human health risk estimation. The authors considered mainly the heavy metal contamination for human health risk estimation due to the availability of reference dose (RfD) and slope factors. In the present paper, the site has been investigated further to quantify the uncertainty in non-



Fig. 1 Location map of Turbhe landfill site



carcinogenic human health risk due to different EBS for multiple population groups using 10,000 MCSs.

Methodology

Materials and methods

Leachate and groundwater samples were collected in 5-L polyethylene bottles from the Turbhe landfill site for laboratory analysis. The leachate samples were collected from the leachate sump at Cell-4 while the groundwater samples were collected from the bore well located near the entrance of the landfill site. The samples were transferred into an icebox immediately after collection and preserved in a cold room (4 °C) until analysis, and the analyses were initiated without any delay. The samples were collected from January to September in 2015. All samples were analyzed for the selected physicochemical parameters, and heavy metals were analyzed according to the standard international procedures specified in APHA (2005). Various physicochemical parameters, including the pH, total dissolved solid (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD), and chloride were monitored for evaluation of LPI. The samples were further preserved for heavy metal analysis with concentrated HNO₃. The heavy metals were analyzed by inductively coupled plasma spectrometry. Nine months of leachate and groundwater data on heavy metals were fitted using all of the parametric distributions in MATLAB R2012a. Further, the best-fit model was selected for the LandSim 2.5 simulation. Table 1 shows the best-fit distribution of the heavy metals data for groundwater and leachate.

To quantify the inherent uncertainty present in human health risks, body weight, water intake, and RfD of heavy metals, data have been collected from various sources. Indian body weight data were collected from the national family health survey (NFHS) (http://rchiips.org/nfhs/), for adults and children. For water intake, U.S. EPA data sets have been adopted in the present study due to unavailability of Indian water intake data. RfD of heavy metals were collected from integrated risk information system (IRIS), health effects assessment summary tables (HEAST), and provisional peerreviewed toxicity values (PPRTV) database. Table 2 shows the RfD and an oral slope factor of heavy metals that are present in the Turbhe landfill leachate.

Engineered barrier system

The EBS for surface and subsurface waste containment comprises components designed to contain, control, and retard the migration of leachate contaminants toward the subsurface. Further, the design is to prevent surface water from infiltrating into the waste and to render waste less harmful to people and the ecosystem for tens of hundreds or thousands of years (NRC 2007). Bonaparte et al. (2002) presented a schematic drawing of an idealized solid waste containment system for solid waste landfill sites. An EBS is used to control the transport of both leachate and landfill gases. EBS components contained bottom barriers, covers and lateral barriers and designed to control advective contaminant migration to promote contaminant retention by mechanisms such as sorption (NRC 2007). Bottom lining systems consisting of a geomembrane, a clay liner, or both are commonly used to contain waste in landfills (Katsumi et al. 2001). The selection of the specific type of liner system required for each type of landfill mainly depends on the kind of a waste. However, leachate transport mechanism also depends on various site-specific factors (soil properties, subsurface characteristics, leachate collection system, water table, and water climatic condition) and extremely difficult to model. Additionally, Katsumi et al. (2001) stated that performance-based analyses are challenged to compare the effectiveness of different landfill liners due to the complexity of chemical transport in landfill liners and involvement of various parameters. In this paper, the heavy metal transport in a no-EBSs context, clay liner, high-density polyethylene (HDPE) liner, and composite liner was reviewed using HHRA as the performance-based analyses for evaluating the landfill bottom-lining system.

The disposal of MSW through open dumping is the most common waste disposal method in most developing countries (Mishra et al. 2016a). Open dumping or no-EBS is the scenario in which the waste is simply dumped on the open lands with no separation between the waste and the environment. However, the probability of human health risks in a no-EBS scenario is very high as the leachate can enter directly into the groundwater. SWM in Indian cities has emerged as a major concern over the past several years. The increase in the urban population and economic growth in the absence of an efficient waste management mechanism has led to the current state of SWM in Indian cities, which is far from a sustainable

Heavy metals	Best fit				
	GW	Leachate			
Fe	Lognormal s = 0.14848, m = 0.01796	Normal m = 148.06, s = 94.382			
Ni	Triangular m = 0.02191, a = -1.8386E-4, b = 0.02194	Normal m = 0.41921, s = 0.12121			
Cr	Uniform a = 0.03631, b = 0.05436	Triangular a = 0.01613, m = 0.488, b = 3.5489			
Cu	Uniform a = 0.03908, b = 0.07313	Normal m = 2.572, s = 1.897			
Co	Uniform a = 0.04134, b = 0.06739	Normal m = 0.39467, s = 0.17171			
Mn	Normal s = 0.03859, m = 0.19318	Uniform a = 0.01767, b = 2.6919			
Zn	Uniform a = 0.0324, b = 0.11503	Lognormal m = 7.7427, s = 6.7532			
В	Lognormal s = 0.22861 , m = -1.8316	Lognormal a = 0.39797, m = 0.398, b = 59.903			

Table 1 Best-fitted distribution of Turbhe ground water and leachate data

management system (Mishra et al. 2016b). Few landfills in India have an EBS with the combination of a leachate collection system and liners (Central Pollution Control Board 2008). Therefore, there is a need to understand the fate and transport of leachate from uncontrolled landfills, which is, unfortunately, the most common solid waste dumping scenario in India.

The primary purpose of the EBS is to isolate the waste from the surrounding environment and, therefore, to protect the soil, surface, and groundwater resources from the pollution originating in the landfill. A single clay liner was considered as the second EBS scenario in this study. This mineral liner is placed so that the primary leachate collection system overlies clay, which acts as a barrier to the leachate flow and attenuates the concentration of the contaminated liquids into the groundwater. A leachate collection system is a protective layer of stone or sand (~0.3 m thick), and a perforated pipe network is sometimes installed within this layer to enhance the drainage of the leachate. A clay liner is a thick, compacted layer of fine-grained soil (0.75–1.0 m thick) that is constructed in the field based on the soil's maximum dry density and optimum moisture content with a maximum hydraulic conductivity of 1×10^{-7} cm/s (Hassan 2014). Natural/local clay is usually

 Table 2
 Reference dose and oral slope factor of heavy metals

used during the construction of landfill liners to avoid the huge cost. However, natural clay is often fractured and cracked. The contaminant transport mechanism through the soil is often modeled numerically by using a dispersion–advection equation. During the investigation of the contaminant transport beneath a landfill, a common assumption is to consider that the soil is saturated. However, it was found that the soil beneath landfills is only partially saturated (Fityus and Smith 1998). Therefore, with proper construction, clay liners can effectively prevent groundwater pollution for a short period.

HDPE liners consist of a clay liner, a geosynthetic clay liner, or a geomembrane made from the specialized plastic sheet (Hughes et al. 2007) and expected to function efficiently for hundreds of years before degradation leads to increased leachate leakage. However, the stabilization of waste usually exceeds the degradation period of HDPE, which results in a sudden rise of leakage of contaminants from landfills after the failure of the liner (Rowe and Sangam 2002). The HDPE liner is a membrane liner in which the primary leachate collection system overlies a geomembrane. HDPE is strong, resistant to nearly all environmental contaminants present in leachate, and considered to be impermeable to water. Therefore, HDPE

Heavy metals	Reference dose (RfD)	Oral slope factor/potency factor	Source
Boron	2×10^{-1}	Studies exhibited that data are insufficient for quantification of carcinogenic risk	IRIS
Chromium (hexavalent ion)	0.003	-	IRIS
Cobalt	3×10^{-4}	_	PPRTV
Copper	4×10^{-2}	_	HEAST
Iron	7×10^{-1}	-	PPRTV
Manganese	1.40×10^{-1}	Not classified as human carcinogen	IRIS
Nickel	2×10^{-2}	Not available	IRIS
Zinc and its compounds	0.3	Inadequate data (there are no reports on the possible carcinogenicity of zinc and compounds for humans)	IRIS

IRIS integrated risk information system, PPRTV provisional peer-reviewed toxicity values, HEAST health effects assessment summary tables

minimizes the transfer of the leachate from the landfill to the environment (Hughes et al. 2007). Katsumi et al. (2001) proposed two primary mechanisms for contaminant transport through the geomembranes, "leakage" through holes and "diffusion" through the geomembrane. Holes and defects in the geomembranes are mostly caused by defects in the geomembrane seams; punctures, caused by the sharp material beneath the membrane liner; tension forces induced by placing waste on the liner; and material failure induced by creep or cyclic loading (Katsumi et al. 2001). Defects such as pinholes, holes, and tears can develop before and after the installation. Giroud and Bonaparte (1989) examined the existence of defects in the geomembrane liner and determined that 8-10 holes/ha are typically present with high-quality assurance and 17 holes/year are usually present when quality assurance is poor. Though quality assurance is excellent, 1-2 holes/ha are inescapable. The properties of HDPE are a function of time, resulting in degradation as time progresses. The single liner should have low permeability and physical strength to withstand both short-term and long-term mechanical stress and strain (Hassan 2014). Carey and Carty (2000) recommend a minimum thickness of 2 mm to provide greater resistance to contaminant breakthrough and increases tear and puncture resistance. Giroud and Bonaparte (1989) proposed a set of equations to calculate the rate of leakage from geomembrane defects.

A composite liner contains a geomembrane in combination with a clay liner. The composite liner utilizes the advantage of both the geomembrane and clay liners; the geomembrane limits the area through which leakage occurs and the clay liner below the geomembrane minimizes the leakage from the geomembrane defects (Katsumi et al. 2001). The composite liner systems are more efficient at restraining the leachate transport into the subsurface compared to either a clay liner or a geomembrane. As a result, leakage from composite liners is often an order of magnitude less than that from single geomembrane and clay liners. The leachate collection system is placed over the composite barrier. Fosse et al. (2001) explained that the flow through composite liners consists of three processes: (1) the leachate movement through the defect in the geomembrane, (2) the flow through an interfacial zone between the geomembrane and soil liner, and (3) the flow through the soil liner. Several studies have focused on predicting leakage rates from composite liners through defects in the geomembrane. However, the most commonly used equations to model contaminant transport have been derived from experimental studies by Giroud (1997) based on the methodology developed in Giroud and Bonaparte (1989). To avoid the leachate leakage, a composite liner is often used as the minimum specified liner system for modern landfills because the hydraulic conductivity of the underlying unsaturated material is replaced with the hydraulic conductivity of the mineral liner.

LandSim: a landfill simulator

Very few studies have been conducted on landfill sites using the LandSim simulation model, which has applications to leachate transport modeling. In Table 3, a comprehensive literature review is presented on the application of the LandSim simulation model worldwide. Plimmer et al. (1999) demonstrated the LandSim simulation over the Burntstump landfill site and proposed a guideline for a probabilistic risk assessment (PRA). Jagloo (2002) examined the transport mechanism of solute contamination from a landfill using the LandSim model and demonstrated the methodology for a landfill in Mauritius. Hall et al. (2006a, b) performed an extensive work from the perspective of the post-closure management of a landfill site. The first comprehensive study was conducted on groundwater RA using LandSim by Slack et al. (2007). In 2011, Butt et al. proposed an integrated and holistic framework for the exposure assessment from the perspective of RA and noted the importance of the LandSim model in estimating pollutant concentrations in groundwater. Palmeri et al. (2012) performed carcinogenic human health risk analyses for the inhalation of volatile compounds present in leachates. The authors claimed that the LandSim model could be used as an integrated tool to assist decision makers in establishing priorities for remediation action. All these studies were conducted and reported on until 2015 and primarily focused on groundwater RA; none of the literature has addressed the issue of modeling the uncertainty in human health risks considering the LandSim-simulated leachate concentrations. To address this lacuna, Mishra et al. (2016b) proposed an integrated approach in the form of a generic framework to quantify the uncertainty that is intrinsic to human health risk estimation. The framework was successfully demonstrated over the Turbhe landfill site in India, and the uncertainties in human health risks were quantified. However, the uncertainty modeling of human health risks with different EBSs still has not been addressed in any of the previous literature.

The LandSim model uses the MCS technique to select randomly from a predefined range of possible input values as the probability density functions (PDFs). It provides lots of control over the input range by considering the uncertainties in the processes, models, and parameters. The PDFs include the uniform, log-uniform, triangular, log triangular, normal, and lognormal (Drury et al. 2003) distributions. The LandSim program can model multiple phases within the same landfill site to predict the cumulative impact of groundwater pollution. The model allows for temporal and spatial variations, but it does not include the quantification aspect of exposure analysis. The model is purely for the landfill assessment of leachate contamination to groundwater, i.e., it does not cover all components of the landfill RA procedure (Butt and Oduyemi 2003). The model provides a long-term forecast of the landfill leachate behavior at each stage of the plume

Sample number	Publication	Major findings/remarks
1	Plimmer et al. (1999)	This study explicitly focused on the theory behind the LandSim simulation, particularly on leachate attenuation and could serve as a guideline for a probabilistic RA using the LandSim model
2	Jagloo (2002)	In this study, groundwater chemistry was evaluated and followed by a water balance to predict the amount of leachate generation. Further, the transport of solute contamination from the landfill was calculated using LandSim. However, the study has not yet performed the exposure assessment and HHRA uncertainty analysis
3	Hall et al. (2006a)	The study primarily focused on the extent of the aftercare period essential by the MSW landfill. This paper suggests that the post-closure management period for a landfill site should be greater than 1000 years depending on the equilibrium state of the pollutants
4	Hall et al. (2006b)	The study revealed that there is no simple relationship between the landfill leachate quality and the equilibrium state. The authors have further shown that the equilibrium status for any landfill is highly site specific and particularly depends on the size of site and depth of waste
5	Slack et al. (2007)	The paper reports the application of the LandSim modeling to evaluate the subsurface contamination of leachate transport from a generic MSW landfill site. This work is the first extensive study that has been performed on groundwater RA using LandSim. However, the human health risk has not yet been estimated
6	Butt et al. (2011)	This paper primarily focused on an integrated and holistic framework of the exposure assessment from the RA perspective. This article also emphasized the use of the LandSim model to estimate the pollutants concentration in groundwater. However, the human health risk and uncertainty associated with HHRA has not yet been quantified
7	Palmeri et al. (2012)	An old MSW landfill site was investigated using LandSim simulation model for the quantification of the long-term risk of groundwater contamination. The purpose was to obtain an integrated tool for assisting policy makers in forming priorities for remediation action. However, the study has not demonstrated the non-carcinogenic health risk estimation and uncertainty estimation
8	Mishra et al. (2016b)	An integral approach in the form of a generic framework is proposed to quantify the uncertainty that is intrinsic to human health risk estimation. This work is the first effort that addresses the issue of uncertainty modeling during HHRA considering the LandSim simulated leachate concentrations

 Table 3
 Comprehensive literature survey on the application of the LandSim simulation model

migration from the source through to the base of the liner, the base of the unsaturated zone, and at the offset monitoring well (Slack et al. 2007). LandSim is a simulation model made for decision making that allows landfill operators and regulators to consider the environmental performance of the geological barrier, artificial liner, and leachate collection systems. It can also consider the large variety of geological and hydrogeological regimes and site-management scenarios.

Human health risk assessment

The HHRA process consists of the following four primary steps: hazard identification, exposure assessment, dose–response assessment, and risk characterization. According to the National Research Council (NRC 1983), "RA is a procedure in which information is analyzed to determine whether a contaminant might cause harm to exposed population or ecosystems." HHRA has been used to quantify public health impacts from contaminated water exposure via multiple exposure pathways and routes (Kentel and Aral 2004). The noncancer health risk is assessed by comparing the disease threshold with the chronic daily intake (CDI). The CDI is the amount or dose of a chemical/agent that enters the bloodstream of members of an at-risk population and is averaged over the number of days for which the population is exposed (Penningroth 2010). Further, the hazard quotient (HQ) is equal to the ratio of the CDI to the RfD. If the HQ (CDI/RfD) is greater than one, i.e., if the exposure exceeds the estimated threshold for a specified non-cancer health effect, then the exposed population is considered to be at risk. If a risk scenario includes several exposure pathways to several chemicals of concern, an HQ is calculated separately, and the outcomes are added together to find the hazard index (HI = $\sum HQ_i$) for those chemicals (Davoli et al. 2010).

Uncertainty in HHRA

Addressing uncertainties in HHRA is a critical issue when evaluating the effects of contaminants on public health (Dong et al. 2015). Uncertainties in HHRA may arise from various sources, such as the measurement/estimation of risk parameters, natural variability in the individual responses of different population groups, variability in the concentration of contaminants over time and space, and assumptions in dose– response models, particularly extrapolations of the results of these models (Kentel and Aral 2004). Uncertainty is inherent in the RA process, even when using the most accurate data and sophisticated models (U.S. EPA 2005). However, qualitative and quantitative uncertainty analysis would enable risk managers to better judge the consequences of different management options (Kalberlah et al. 2003). Recently, PRA studies have become popular for analyzing the uncertainty and variability associated with the parameters of risk equations (Kentel and Aral 2004). PRA effectively combines risk characterization with uncertainty analysis by providing the range of possible risk values (Stackelberg and Burmaster 1994). PRA, particularly Monte Carlo analysis, which uses statistical tools, is currently the most common method for evaluating uncertainty and variability in health RA (Schuhmacher et al. 2001). Keeping the importance of uncertainty modeling in mind, the MCS framework proposed by Mishra et al. (2016b) was applied in the present study to model the uncertainty of human health risks associated with MSW landfill leachate contamination for different EBSs.

Results and discussion

To evaluate the overall status of the landfill leachate, the widely accepted pollution index developed by Kumar and Alappat (2003) was applied in the present study. The LPI of the Turbhe landfill leachate was estimated and can be considered as a preliminary step of HHRA. The leakage rates in four selected EBS scenarios have been simulated using the LandSim simulator. The uncertainty associated with the non-carcinogenic human health risk was quantified using the framework proposed by Mishra et al. (2016b) for six heavy metals under four EBS scenarios. Further, the uncertainty analysis was performed considering Indian body weight data, which were collected from NFHS and USEPA water intake data adopted from Roseberry and Burmaster (1992).

Leachate pollution index

Kumar and Alappat (2003) developed a procedure to quantify the leachate contamination strength of landfills on a relative scale in terms of the LPI. The LPI is an increasing scale index, wherein a higher value indicates a poor environmental condition. In the process of HHRA, LPI can be considered as a hazard identification step. The LPI can be used to represent variation in leachate quality for a specific landfill site over time. The trend analysis so developed for any landfill can be used to design the leachate treatment facility and assess the post-closure monitoring periods. LPI is like a grade ranging from 5 to 100 that expresses the overall leachate contamination potential of a landfill site at a given time. The level of LPI ranges from 5 to 100, where 5 indicates good environmental condition and 100 indicate worst environmental condition. The age of the landfill site dominantly governs the leachate characteristics and hence LPI values. The high value of LPI indicates that the leachate generated from the dumping site is not stabilized (Kale et al. 2010).

The LPI of 10 parameters of Cell-4 leachate has been calculated for mean and maximum concentration based on Delphi techniques as shown in Table 4. The weighting to each variable is given according to their significance level and the total of variable weighting is 0.543. For Cell-4 leachate, when the mean and maximum concentration of leachate pollutants was taken into consideration, the LPI is found to be 23.85 and 30.05, respectively. As per the MSW (Management and Handling) Rules, 2000, the LPI value is determined to be 7.378 for leachate disposal standards to inland surface water. Further, the landfill site has been accepting the solid waste without any proper segregation. The moderately high value of LPI indicates contamination in Turbhe landfill, which can pose a greater risk to public health particularly population residing near the site.

Comparison of leachate leakage through EBS

The present study simulates leachate leakage through four EBSs using multiple LandSim simulations. The model uses a contaminant-specific declining source term based on the results of the standard up-flow percolation leaching tests, and the Laplace transform technique is used to solve the advection-diffusion contaminant transport equation (Carey and Carty 2000; Slack et al. 2007). The LandSim model calculates the head of the leachate in the landfill, considering that the infiltration and drainage system is fixed to a specified head for a period, before ending the management control of the site. LandSim also calculated the leachate flow rate through the landfill base, based on the leachate head and the presence of any engineered barrier. The leachate leakages from the four EBSs have been calculated using multiple LandSim simulations (Fig. 3). The plot shows that the leakage was high for the no-EBS scenario with 15,255 l/day during an active life of 5 years. This value dropped suddenly from its closure to the end of management control period (30 years), and in the long run, the value showed an increasing trend. The single clay liner demonstrated a leakage of 2000 l/day until the end of the management control period and later increased to its maximum value within 120 years of this period, which can be considered the service life of clay liners (Rowe and Fraser 1994). The composite and HDPE liners also showed better performance with minimum leakage values of 42 and 210 l/ day, respectively, until 30 years. A significant increase of leakage usually occurs at the time of the cessation of management control, and the head on the liner will suddenly rise when the head is no longer controlled at the compliance limit by pumping. After 30 years of managed control, few peaks and undulations have been observed in the HDPE liner simulation. This phenomenon might be due to a change in the statistical distribution of the defects in the liner over time. The number of defects is predicted to increase every 30 years from 0 to 150 years as the "most likely" value in the distribution migrates upward. Afterward, the growth in the hole size and leakage rates increase exponentially until these factors reach

Pollutant	Pollutant weight (w_i)	Pollutant average concentration (c_i) (mg/l)	Sub-index score (p_i)	LPI $(w_i \cdot p_i)$ (average)	Pollutant maximum concentration (c_i) (mg/l)	Sub-index score (p_i)	LPI $(w_i \cdot p_i)$ (maximum)
Chromium	0.064	0.455	5	0.32	0.748	6	0.384
COD	0.062	10,330.1	75	4.65	12,852	76	4.712
BOD	0.061	5524.06	58	3.538	6542	62	3.782
Zinc	0.056	0.702	5	0.28	1.032	5	0.28
pН	0.055	8.015	3	0.165	8.68	4	0.22
Nickel	0.052	0.347	5	0.26	0.504	6	0.312
TDS	0.05	12,173.9	24	1.2	23,300	50	2.5
Copper	0.05	0.272	5	0.25	0.708	6	0.3
Chloride	0.048	5007.95	43	2.064	7980	75	3.6
Iron	0.045	7.579	5	0.225	18.188	5	0.225
Total	0.543			12.952			16.315
Final overall pollution $\sum (w_i, p_i) / \sum w_i$				23.852			30.046

the maximum defined by the underlying material. In the model, the time for the size of the defect to double is considered to be 100 years and the degradation time is 150 years. The composite liner performed best, i.e., showed a maximum leakage of 14,400 l/day only after the 180-year period.

Contaminant time history

LandSim probabilistically estimates the possible concentration of pollutants at different levels that can reach a given point on the ground over a period. The present study calculates the concentration of pollutants in the groundwater near the landfill site using LandSim. The Cell-4 of the Turbhe landfill site was selected for the LandSim simulation. The initial concentrations of heavy metals in the Cell-4 leachate were estimated in laboratory analyses. Further, the various input parameters were collected for multiple LandSim simulations. The compliance point was fixed at a distance of 500 m, and the concentrations of heavy metals (B, Co, Cr, Cu, Fe, Mn, Ni, and Zn) at the compliance point were simulated and predicted for future years. A comparison of these



Fig. 3 Comparison of leachate leakage through different EBS

predictions for the different liner types is shown in Fig. 4. As the composite liner is a combination of a clay liner and HDPE, it performs best in preventing contaminant migration. The clay liner outperforms the HDPE liner, in the long run, because of its cation exchange capacity and the partition coefficients k_d of contaminants in clay. Although the hydraulic conductivity of HDPE is very low compared to the clay liner, this factor reduces the advective transport, but it cannot prevent the diffusive transport. For the long-term performance of the liners, the order of performance in preventing contaminants migration is the composite > clay liner > HDPE > no-EBS.

Quantification of uncertainty in HHRA

The present study considered four EBS scenarios to quantify the performance of the barrier systems from the HHRA perspective. The uncertainty involved in the body weight, daily water intake, and pollutant concentrations (primarily from heavy metals) was considered and the uncertainty in the risk output values is shown. The 20-64 age groups were defined as adults and the 1–10 age groups as the children population; the body weight data in India were collected from the NFHS for all of India. A set of nonparametric kernel distributions was fitted on the collected demographic data. The best kernel function was selected based on the minimum RMS value. The normal smoothing function was found to be best fitted for the adults and children population groups with the minimum RMSE value. For the water intake distribution in this study, U.S. EPA data sets were adopted due to a lack of availability of Indian water intake data. For the uncertainty analysis, an MCS (with 10,000 iterations) framework developed by Mishra et al. (2016b) was adopted and conducted by considering the metal concentrations, human body weights, and daily water intakes as the uncertain parameters. The Turbhe



Fig. 4 Simulated contaminants concentration from LandSim

landfill site was simulated, and the non-carcinogenic human health risk was calculated using the LandSim-simulated heavy metal concentrations. The non-exceedance probability distributions of the HQ for six heavy metals (Co, Cu, Mn, Ni, Zn, and Fe) were quantified for the four selected EBS scenarios for adults and children. To simulate the long-term performance, the HI values were plotted for 5, 50, 100, and 200 years as shown in Figs. 5 and 6. The result shows the nonexceedance probability distribution of HI for eight heavy metals (B, Co, Cr, Cu, Mn, Ni, Zn, and Fe) for the adults (Fig. 5) and for the children (Fig. 6) population with different liner systems at various time slices. Out of the eight heavy metals, the HQ values for Co were found to be at the maximum (>1) for every time slice, which indicates the presence of a high concentration of Co in leachate for all population groups. The HI values were found to be increasing from 5 to 200 years. For the male population, the HI value varied from 0.5 to 15, while for children, this value ranged from 3 to 25 (Fig. 5). A significant variation in the potential for risk was observed in the 100- and 200-year plots. For example, the 100-year plot in Fig. 5 shows that there is a 90% chance that the risk is less than the HI value of three in the composite liner scenario, while there is an 80% chance that the risk index is less than three for the clay and HDPE liners; in the case of the no-EBS scenario, this chance is 60%. Similar conclusions can be drawn from all the other plots, and this comparison will lead to good decision making in choosing a liner based on its performance in the long run.

Conclusions

Economic considerations ensure that landfills will remain to be one of the most common waste disposal methods, regardless of the enormous amount of leachate generation that poses a significant threat to the surrounding environment and, subsequently, to human health. The human health risks due to the possible consumption of groundwater from leachate contamination must be quantified with a RA tool. Landfill technology has undergone significant developments in the last several decades, i.e., developing from open dumps to highly engineered structures. However, these engineered structures can still pose a threat to surface and groundwater resources. The flow and transport of leachate contaminants reaching the groundwater are very site specific and depends on numerous parameters such as the geology, precipitation, soil properties, and type of EBS. In the present study, an effort was made to quantify the uncertainty in human health risk due to MSW landfill leachate contamination under different EBS scenarios using the LandSim 2.5 simulation model. Further, the uncertainty in human health risks due to MSW landfill leachate contamination was quantified using an HHRA approach as proposed by the NRC. The present study is the first to quantify the uncertainties in human health risks due to the intake of leachate-contaminated groundwater for different EBSs using the LandSim model. To achieve this goal, the Turbhe landfill site in Navi Mumbai, India, was selected to depict existing dumping scenarios in India. Nine months of continuous monitoring was performed, and heavy metal concentrations were estimated. Multiple LandSim simulations were performed using Monte Carlo simulation to quantify the risk index HI for various EBS scenarios. The RA reveals a high risk to children compared to the adult population. The HI values were found to be in decreasing order compared to the no-EBS system. However, the RA studies are highly site specific and so must be conducted for each landfill site for the proper solid waste management program. The principal findings of the current study are presented below:

 The leachate leakage values showed that the liners were extremely effective in obstructing leachate flow till the management control period (30 years). However, in the long run, the leakage through the clay liner, HDPE liner, and composite liner reached its maximum value after 120,

Fig. 5 Comparison of health risk for adult population: **a** 5 years, **b** 50 years, **c** 100 years, **d** 200 years



150, and 180 years, respectively. These were very close to the service life of the liners mentioned in the literature.

2. The RA performed on the Turbhe landfill reveals a high risk to children (HI values from 3 to 25) compared to the adult population (HI values from 0.5 to 15) with the performance level of liners in the order of the composite >

clay liner > HDPE > no-EBS. In this study, the composite liner outperforms the clay, HDPE, and no-EBS by 10, 10, and 25%, respectively.

3. The long-term monitoring of any landfill site requires enormous capital, manpower support, and expertise on solid waste management systems. Additionally,





quantification of human health risks is not straightforward in terms of calculating the risk values. It is data extensive and site specific and may be varied worldwide, depending on several factors such as the landfill age, waste category, available leachate treatment facility, geology, soil properties, and type of EBS. Therefore, the EBS selection must be based on scientific study considering all the variables in LandSim.

The long-term performance of EBSs is monitored indirectly, which is usually evidence of contaminant migration to the surface and groundwater. The literature suggests that existing simulation models are efficiently simulating long-term performance. However, municipalities must develop a monitoring program for new and existing facilities to collect data for assessing the long-term EBS performance and future research must consider both barrier performances and the adverse effects to public health through RA studies.

References

- APHA (2005) Standard methods for the examination of water and wastewater, 21st edn. American Public Health Association, Washington, DC
- Asnani PU (2006) Solid waste management. India infrastructure report 570
- Bonaparte R, Daniel D, Koerner RM (2002) Assessment and recommendations for improving the performance of waste containment systems. Environmental Protection Agency
- Butt TE, Clark M, Coulon F, Oduyemi KO (2009) A review of literature and computer models on exposure assessment. Environ Technol 30(14):1487–1501. https://doi.org/10.1080/09593330903345952
- Butt TE, Gouda HM, Baloch MI, Paul P, Javadi AA, Alam A (2014) Literature review of baseline study for risk analysis—the landfill leachate case. Environ Int 63:149–162. https://doi.org/10.1016/j. envint.2013.09.015
- Butt TE, Ingles AJD, Baloch MI (2011) A conceptual model outline for integrated exposure assessment of waste disposal sites. Environ Prog Sustain Energy 30(4):696–708. https://doi.org/10.1002/ep. 10526
- Butt TE, Lockley E, Oduyemi KOK (2008) Risk assessment of landfill disposal sites—state of the art. Waste Manag 28(6):952–964. https:// doi.org/10.1016/j.wasman.2007.05.012
- Butt TE, Oduyemi KOK (2003) A holistic approach to concentration assessment of hazards in the risk assessment of landfill leachate. Environ Int 28(7):597–608. https://doi.org/10.1016/S0160-4120(02)00100-9
- Carey P, Carty G (2000) Landfill manuals: landfill site design. Environmental Protection Agency, Ireland
- Central Pollution Control Board (2008) Guidelines and check-list for evaluation of MSW landfills proposals with information on existing landfills. Available at: http://cpcb.nic.in/upload/NewItems/ NewItem_133_MSW-REPORT.pdf, Accessed January 2017
- Chourey P, Yatish L, Tomar S, Dessai P (2014) Environmental status report of Navi Mumbai municipal corporation 2013-14. TERI p 157
- Christensen TH, Kjeldsen P, Bjerg PL, Jensen DL, Christensen JB, Baun A, Albrechtsen HJ, Heron G (2001) Biogeochemistry of landfill

leachate plumes. Appl Geochem 16(7):659–718. https://doi.org/10. 1016/S0883-2927(00)00082-2

- Davoli E, Fattore E, Paiano V, Colombo A, Palmiotto M, Rossi AN, Il GM, Fanelli R (2010) Waste management health risk assessment: a case study of a solid waste landfill in South Italy. Waste Manag 30(8):1608–1613. https://doi.org/10.1016/j.wasman.2009.10.013
- Dong Z, Liu Y, Duan L, Bekele D, Naidu R (2015) Uncertainties in human health risk assessment of environmental contaminants: a review and perspective. Environ Int 85:120–132. https://doi.org/10. 1016/j.envint.2015.09.008
- Drury D, Hall DH, Dowle J (2003) The development of LandSim 2.5. NGCLC Report GW/03/09. Environment Agency, Solihull
- FICCI (2009) Survey on the current status of municipal solid waste management in Indian cities and the potential of landfill gas to energy projects in India. Available at: https://www.globalmethane.org/Data/ 292 2 ficci survey 09.pdf, Accessed January 2017
- Fityus SG, Smith DW (1998) Modelling of a geomembrane in a landfill liner. In Proceedings of the 3rd International Congress on Environmental Geotechnics, Lisbon, Portugal, 2:807–812
- Foose GJ, Benson CH, Edil TB (2001) Predicting leakage through composite landfill liners. J Geotech Geoenviron 127(6):510–520. https:// doi.org/10.1061/(ASCE)1090-0241(2001)127:6(510)
- Giroud JP (1997) Equations for calculating the rate of liquid migration through composite liners due to geomembrane defects. Geosynth Int 4(3–4):335–348
- Giroud JP, Bonaparte R (1989) Leakage through liners constructed with geomembranes—part I. Geomembrane liners. Geotext Geomembr 8(1):27–67. https://doi.org/10.1016/0266-1144(89)90009-5
- Hall DH, Drury D, Gronow JR, Rosevear A, Pollard SJ, Smith R (2006a) Estimating pollutant removal requirements for landfills in the UK: I. Benchmark study and characteristics of waste treatment technologies. Environ Technol 27(12):1309–1321. https://doi.org/10.1080/ 09593332708618753
- Hall DH, Drury D, Gronow JR, Rosevear A, Pollard SJ, Smith R (2006b) Estimating pollutant removal requirements for landfills in the UK: II. Model development. Environ Technol 27(12):1323–1333. https://doi.org/10.1080/09593332708618754
- Hassan AA (2014) Hydraulic performance of compacted clay liners (CCLs) under simulated landfill conditions. Doctoral dissertation, Carleton University Ottawa.
- Hoornweg D, Bhada-Tata P (2012) What a waste: a global review of solid waste management. Urban development series knowledge papers 15:1–98
- Hughes KL, Christy AD, Heimlich JE (2007) Landfill types and liner systems. Ohio State University Extension Fact Sheet CDFS-138
- Jagloo K (2002) Groundwater risk analysis in the vicinity of a landfill: a case study in Mauritius. Royal Inst. of Technology
- Kalberlah F, Schneider K, Schuhmacher-Wolz U (2003) Uncertainty in toxicological risk assessment for non-carcinogenic health effects. Regul Toxicol Pharmacol 37(1):92–104. https://doi.org/10.1016/ S0273-2300(02)00032-6
- Kale SS, Kadam AK, Kumar S, Pawar NJ (2010) Evaluating pollution potential of leachate from landfill site, from the Pune metropolitan city and its impact on shallow basaltic aquifers. Environ Monit Assess 162(1–4):327–346. https://doi.org/10.1007/s10661-009-0799-7
- Katsumi T, Benson CH, Foose GJ, Kamon M (2001) Performance-based design of landfill liners. Eng Geol 60(1):139–148. https://doi.org/10. 1016/S0013-7952(00)00096-X
- Kentel E, Aral MM (2004) Probabilistic-fuzzy health risk modeling. Stoch Env Res Risk A 18(5):324–338. https://doi.org/10.1007/ s00477-004-0187-3
- Kumar D, Alappat BJ (2003) Analysis of leachate contamination potential of a municipal landfill using leachate pollution index. Workshop on Sustainable Landfill Management, pp:147–153

- Kumar S, Bhattacharyya JK, Vaidya AN, Chakrabarti T, Devotta S, Akolkar AB (2009) Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: an insight. Waste Manag 29(2):883–895. https://doi.org/10.1016/j.wasman.2008.04.011
- Mishra H, Karmakar S, Kumar R, Singh J (2016b) A framework for assessing uncertainty associated with human health risks from MSW landfill leachate contamination. Risk Anal 37(7):1237– 1255. https://doi.org/10.1111/risa.12713
- Mishra H, Rathod M, Karmakar S, Kumar R (2016a) A framework for assessment and characterisation of municipal solid waste landfill leachate: an application to the Turbhe landfill, Navi Mumbai, India. Environmental Monitoring and Assessment, 188(6), 357(1– 26)
- National Research Council (1983) Risk assessment in the Federal Government: managing the process. Committee on the institutional means for assessment of risks to public health. In: Commission on life sciences. National Academies Press, Washington, DC
- National Research Council (2007) Assessment of the performance of engineered waste containment barriers. National Academies Press
- Navi Mumbai Municipal Corporation (2010) Navi Mumbai environmental plan for clean, green and healthy city, environmental status report. Available at: http://www.nmmconline.com/documents/10156/ 40405/2.summary.pdf, Accessed January 12, 2016
- Navi Mumbai Municipal Corporation (2013) Solid waste management, environmental status report. Available at: http://www.nmmconline. com/c/document_library/get_file?uuid=a51d91c6-19ad-40eb-a75ebde50a58ef2e&groupId=10156, Accessed January 12, 2016
- Palmeri E, Mancini G, Luciano A, Viotti P (2012) Risk analysis of a disused landfill as support tool for defining strategy and priority of the remediation actions. Chemical Engineering Transaction 28:43– 48
- Penningroth S (2010) Essentials of toxic chemical risk science and society, 1st edn. Boca Raton FL CRC Press, New York. https://doi.org/ 10.1201/9780203022627
- Plimmer BR, Pringle AB, Moncaster SJ (1999) A probabilistic risk assessment methodology for landfills, with particular reference to the

representation of chemical containment. Geol Soc Lond, Spec Publ 157(1):275–280. https://doi.org/10.1144/GSL.SP.1999.157.01.19

- Rathod M, Mishra H, Karmakar S (2013) leachate characterization and assessment of water pollution near municipal solid waste landfill site. Int J Chem Phys Sci 2013; Vol. 2, Special Issue
- Roseberry AM, Burmaster DE (1992) Lognormal distributions for water intake by children and adults. Risk Anal 12(1):99–104. https://doi. org/10.1111/j.1539-6924.1992.tb01312.x
- Rowe RK, Fraser MJ (1994) Consideration of uncertainty regarding service lives of engineered systems in assessing potential contaminant impact. CSCE Special Publication—Engineering Materials for Waste Isolation, pp. 119–146
- Rowe RK, Sangam HP (2002) Durability of HDPE geomembranes. Geotext Geomembr 20(2):77–95. https://doi.org/10.1016/S0266-1144(02)00005-5
- Schuhmacher M, Meneses M, Xifró A, Domingo JL (2001) The use of Monte-Carlo simulation techniques for risk assessment: study of a municipal waste incinerator. Chemosphere 43(4):787–799. https:// doi.org/10.1016/S0045-6535(00)00435-5
- Slack RJ, Gronow JR, Hall DH, Voulvoulis N (2007) Household hazardous waste disposal to landfill: using LandSim to model leachate migration. Environ Pollut 146(2):501–509. https://doi.org/10.1016/ j.envpol.2006.07.011
- Slack RJ, Gronow JR, Voulvoulis N (2005) Household hazardous waste in municipal landfills: contaminants in leachate. Sci Total Environ 337(1):119–137. https://doi.org/10.1016/j.scitotenv.2004.07.002
- Stackelberg KV, Burmaster DE (1994) A discussion on the use of probabilistic risk assessment in human health impact assessment. Environ Impact Assess Rev 14(5):385–401. https://doi.org/10. 1016/0195-9255(94)90009-4
- Talalaj IA, Biedka P (2016) Use of the landfill water pollution index (LWPI) for groundwater quality assessment near the landfill sites. Environ Sci Pollut Res 23(24):24601–24613. https://doi.org/10. 1007/s11356-016-7622-0
- U.S. EPA (2005) Guidelines for carcinogen risk. U.S. EPA, Washington, DC. EPA/630/P-03/0018