

**IDENTIFICATION OF GROUNDWATER CONTAMINATION AND  
DEVELOPMENT OF SITE-SPECIFIC PERMEABLE REACTIVE  
BARRIER SYSTEM FOR ENVIRONMENTAL POLLUTION  
CONTROL OF OPEN SOLID WASTE DUMPSITES IN SRI LANKA**

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A dissertation submitted in partial fulfillment of the requirements for  
the degree of

**Doctor of Philosophy**

In environmental and Infrastructure Engineering  
to the

Graduate school of science and Engineering  
SAITAMA UNIVERSITY

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September 2018

## **Acknowledgement**

To my supervisor, Prof. Ken Kawamoto: because he is an excellent teacher. The door to Prof. Kawamotos' office was always open whenever I ran into a trouble spot or had a question about my experiments or writing. Many thanks.

To Dr. Takeshi Saito: for the continuous support for the experiments, kind attention, and valuable advice. Thank you very much.

To Dr. Sakamoto, AIST, Japan, for his continuous and kind guidance on GERAS model simulation. Many thanks.

To the committee members, Prof. Noriko Tanaka, Prof. Masahiko Osada, Dr. Shingo Asamoto, Saitama University, Japan and Dr. Yushide Sakamoto, AIST, Japan for their valuable comments and suggestions on my study. Thank you very much.

To Prof. Komatsu: because she was a good teacher and a nice friend that I have ever met. She encouraged me in my research career and life matters. I learned many things from her during my stay in Japan and I also love her lovely cat LB. I am really going to miss you both.

To my eternal cheerleader, Prof. M.I.M. Mowjood: for encouraging me to be a cheerful researcher. Thank you very much.

I am also grateful to the following university staff: Mr. Matsuno, Mr. Kunihiro Kobayashi, Ms. Enamoto, Ms. Yoko Mori, Ms. Minori Ichimaru and Ms. Chizuko Sato for their priceless support.

All the Japanese, international and Sri Lankan friends: because they helped me in a numerous way and shared my sorrow, happiness, and joy together. And my special thanks

to Mr. Rui Saito and Yuki Katayama; co-members of my research, for their dedicated and careful laboratory work. I greatly appreciate.

To Dr. Masato and his family: for being really good friends to me and my family. They were pretty behind us in our every life matter during our stay in Japan. Many thanks for your assistance.

To the Japanese Ministry of Education, culture, sports, science, and technology: for selecting me as a Munbukagakusho scholar. It was really a good support to finish my Ph.D. successfully.

A very special gratitude goes out to the SATREPS project, for helping and providing funds for the experiments.

Last but by no means of least my dearest thanks to my husband, little daughter, my parents, and relations, for making my study period really comfortable and relax.

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## **Chapter 01. GENERAL INTRODUCTION**

### **1.1 Background**

Portable groundwater resources throughout the world are contaminating in an accelerated way as a part of negative impacts of the economic development, rapid population growth, revolutions in patterns in consumptions of goods and services, and the poor human perception on the environmental conservation etc (B.J. Alloway, 2013; Grimm et al., 2008; Mulligan et al., 2001). The underground water resources change their chemical composition, once it changes the quality due to the mixing of inert toxic contaminants (Naftz and Davis, 1999). The contaminants create a plume within an aquifer and spread over a wide area due to the movement of water and dispersion of inert materials. Finally, the advances boundaries, such as groundwater wells and springs, bring contaminated groundwater which is unsafe to use by human and other flora and fauna. The primary sources of groundwater pollution have been identified as improper management of underground chemical storage, leaking of sewage tanks, improper management of mining sites and less care in solid waste management etc (Grimm et al., 2008).

Inter alia, the poor management of municipal solid waste has become a serious threat to the groundwater quality, all over the globe (Hoornweg and Bhada-Tata, 2012). Especially in developing countries the primitive steps of waste hierarchy; (waste minimization, resources recovery, waste to energy and energy recovery) is frequently missing (fig. 1.1) and the large proportion of the municipal solid waste is dumped into the open areas as the primary and final step of the waste management. According to the Trankler et al., (2005) 90% of municipal solid waste produced all over the world is disposed of in un-engineered landfills. The open dumping of waste is more popular in developing countries due to its easiness and low cost in management. In Sri Lanka too, the primary waste management

practice is the open and control dumping, unfortunately, none of these dumpsites are engineered or sanitary landfills. Further, the waste generation is increasing in a rapid way, and the future waste generation in the year 2025 is expected to be 1.0 kg/capita/day in Sri Lanka (Wijesekara et al., 2014). Thus the number of the open solid waste dumpsites will be increased in the future; this might create a greater risk of groundwater pollution nearby the open dumpsites as the absence of the proper waste management practices.

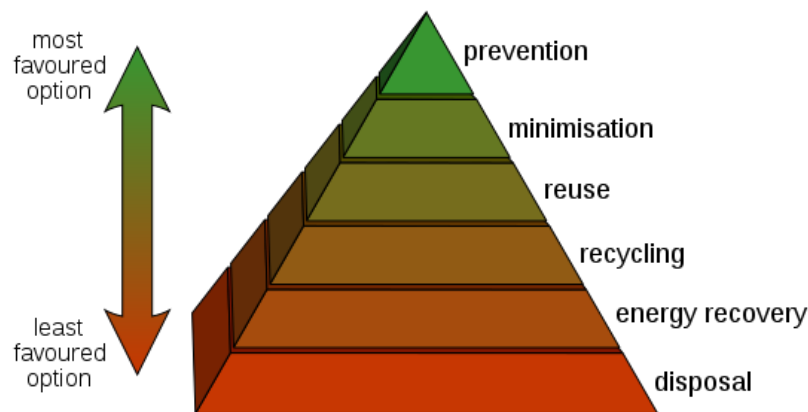


Figure 1-1 The waste hierarchy

Source: [https://en.wikipedia.org/wiki/Waste\\_hierarchy](https://en.wikipedia.org/wiki/Waste_hierarchy)

During the decomposition of the dumped waste, the landfill leachate generated by excess rainwater percolating through the waste layers. Further, water coming out from the waste materials and the water squeezed out from the waste materials also contributes to the leachate generation. The landfill leachate contains various types of pollutants, since the dumped waste contains different types of household wastes, non-hazardous industrial wastes etc. Landfill leachate is a very concentrated solution having high Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), inorganic ions, xenobiotic compounds, heavy metals (Christensen et al., 1998). Density of leachate is also higher than water ( $\sim 1.14 \text{ kg/L}$  at  $10^\circ\text{C}$ ) due to the presence of huge loading of salts. Leachate consists of different organic matter such as humic acid, fulvic acid and inorganic compounds that may be either dissolved or suspended (Hamidi *et al.*, 2014). Heavy metals may release by

waste such as ceramics, electronic wastes, batteries, debris of motor mechanic industry etc. High concentrations of Cd, Hg, Ni, Mn, Cu and Pb have been reported from leachate collected at many open dumpsites (Chen., 1996 ; Udayagee et al., 2017; Wijesekara et al., 2014)). Table 1.1 exemplify some heavy metal concentrations observed from different open solid waste dumpsites in Sri Lanka. In some cases the observed heavy metal concentrations exceeded the maximum effluent water quality standards (Sewwandi et al., 2013). The leachate quality varies greatly, from place to place region to region, and with respect to the age of the dumping, management practices at the dumpsites, the degree of the waste compaction, climatic factors, site hydrology etc. This toxic leachate may easily seep into the underground water bodies since the open dumpsites are the absence of any barrier materials such as liners.

Many groundwater contamination incidents have been reported at open dumpsites and their surroundings, caused by leachate (Mor *et al.*, 2006; Abbas *et al.*, 2009). Further, the landfill leachate toxic to higher plants, algae, human beings and other animals (Natale; 2008). As an example ammonia presents in leachate at high concentrations can cause considerable toxic effects to fish and other aquatic fauna (Christensen *et al.*, 2001). Especially, once the heavy metals reach to the groundwater bodies, the bioaccumulation may occur and it leads several health issues such as kidney diseases, cancers, mental retardation in children, gastrointestinal disorders etc.

Thus the onsite monitoring is essential to evaluate the current level of the contamination and the future the risk of groundwater pollution. Once identified the future risk, the next step to be implementation of the treatment facilities to avoid the mixing up of leachate with underground water bodies. But, it has become a challenge to treat the leachate, since the open solid waste dumpsites are absence of the leachate collection facility. Thus, the in-

situ treatment of groundwater has been identified as the best option to remediate the groundwater pollution surrounded by the open solid waste dumpsites.

Conventional pump-and-treat methods, combining groundwater extraction used widely all over the globe to treat contaminated groundwater in past few decades (Naftz and Davis, 1999). The applicability of these methods has become limited in developing countries due to some economic and technical issues, thus the locally usable low-cost treatment facility is highly demanded in this regard (USEPA, 1999).

Table 1-1 The heavy metal toxicity of leachate generate at different open solid waste dumpsites in Sri Lanka  
The values are given in ppb. \*- higher than the maximum permissible levels.

Climatic zone of Sri Lanka	Sample location	Cr	Fe	Ni	Cu	Zn	As	Se	Cd	Pb
Wet zone	Bandaragama	329*	7167*	912	227	5362*	722*	2607*	90	479*
	Gampola	220*	5546*	335	734	462	164	461	4	34
	Gohagoda	470*	77000*	1900	190	6600*	170	220	20	500*
	Rathnapura	439*	56343*	1311	627	1685	1551*	4922*	52	168*
	Kolonnawa	1968*	346930*	4473*	55	11759*	705*	2443*	15	421*
	Galle	486*	15477*	673	564	593	1796*	5947*	52	169*
Intermediate Zone	Wennapuwa	363*	2501	399	431	409	939*	2812*	53	87
	Negombo	330*	20111*	666	535	2062*	846*	2184*	51	333*
	Matale	345*	60762*	115	573	6876*	522*	1935*	100*	1777*
Dry Zone	Hambantota	80	5341*	226	166	19909*	678*	2522*	172*	492*
	Kataragama	11	1117	89	58	638	106	400	50	123*
Max. permissible level		100	3000	3000	3000	5000	200	500	100	100

Source: (Sewwandi et al., 2013)

The permeable reactive barrier (PRB) systems arrived recently as an inexpensive and promising technology in groundwater treatment. The concept behind the PRB is trapping and immobilization of contaminants in groundwater, inside the barrier constructed across the contaminated water flow path. The main advantage of the PRB is the passive nature of the treatment process; the barrier is only a barrier to the contaminant, not for the groundwater flow. Thus the environmental impact of the facility is minor and identified as an eco-friendly system (Carey et al., 2002; Obiri-Nyarko et al., 2015; Regmi, 2009). Fig.1.2 illustrates the groundwater treatment process by PRB.

Basically, two types of PRBs installation configurations exist as continuous walls and gate barriers. The funnel and gate system uses impermeable gates to alter the groundwater flow and to direct the contaminant plume towards the PRB, whereas the continuous PRB completely transect the plume flow path with the reactive media (Smith et al., 2003; Thiruvengkatachari et al., 2008). It is important to keep the reactive zone permeability equal to or greater than the permeability of the aquifer to avoid the diversion of the flowing water flow direction (Statham et al., 2015; Turner et al., 2008).

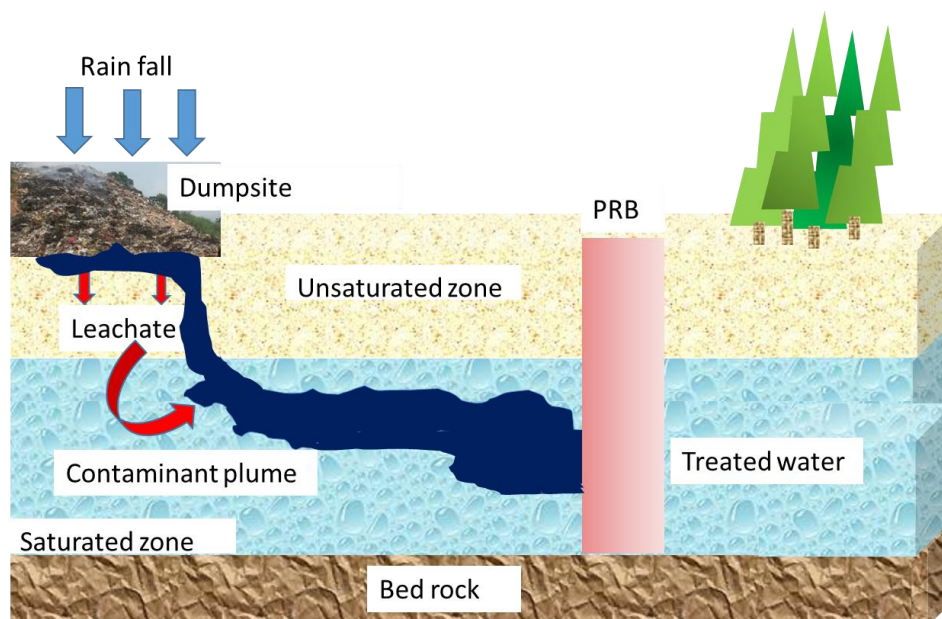


Figure 1-2 The groundwater treatment process by PRB



Thus the selection of PRB filling materials should be done in a scientific way; the filling materials should have greater capacity of immobilization of targeted contaminant, low leaching capacity, and high permeability (Smith et al., 2003; Thiruvengkatachari et al., 2008; Vignola et al., 2011). A numerous kind of contaminants have been tested in laboratory level and some of those have been used in actual field applications (Statham et al., 2015). Zero-valent iron (ZVI),  $\text{Fe}^0$ , has been used widely as a PRB material (Statham et al., 2015; Suzuki et al., 2012), and as reported in ITRC (2005), more than 60% of PRBs were made of ZVI by 2004.

Further, activated carbon (US Environmental Protection Agency, 1999), zeolite (Vignola et al., 2011), soil-bentonite (US Environmental Protection Agency, 1999) mixtures have been used widely in field applications.

Several biomaterials have been tested for their adsorption capacities in laboratory level batch experiments to evaluate their adsorption capacities towards the targeted contaminants. Some biomaterials such as coconut husk powder (Sewwandi et al., 2014), crab shells (Vijayaraghavan et al., 2011), peanut shells (Han et al., 2011), sawdust (Sewwandi et al., 2012), activated neem leaves (Babu and Gupta, 2008), and coir pith (Parab et al., 2006) have been recognized as potential low-cost adsorbents in PRB systems due to their high performances in heavy metal removal from wastewater. Further, the long term performances evaluations of reactivity and water flow properties have been examined by using different reactive media such as organic carbon (US Environmental Protection Agency, 1999), Zero valent iron (Tratnyek, 1997), zeolite (Regmi, 2009) by conducting field and laboratory column experiments. Table 1.2 summarized some of those studies conducted to evaluate the performances of PRB reactive media.

Even though plenty of researches carried out to evaluate the reactivity of PRB filling media, a research gap has been found a complementary study on evaluation of both reactivity and hydraulic performances of the PRB filling materials. Thus, both the reactivity and hydraulic performances of suggested PRB filling materials should be critically evaluated by conducting both batch and column studies at laboratory level, before move into field installations.

Table 1-2 Past studies conducted on PRB

PRB material	Pollutant of interest	Scale	Country	Reference
Olive husk Cow manure	Pb, Zn and Cu	Lab scale	-	Ok <i>et al.</i> , 2010.
Poultry litter	Pb, Cu	Lab scale	Japan	Hashimoto <i>et al.</i> , 2009
Bone apatite material (Contain HAP)	Uranium	Lab scale	California	Fuller et al., 2003
Fe <sup>0</sup>	hydrocarbon	Field scale	-	Tratnyek, 1997
Silica sand + Ca crushed limestone + readily available metal oxides	Phosphate	Lab scale (batch & column)	Canada	Blowes et al., 1997
Volcanic ash soil + Fe powder + molten slag	pH, EC, organic pollutants, inorganic ions, metals	Lab scale (lysimeter)	Japan	Ono et al., 2008
Freshwater microalgae, Raw plant, Freshwater crustacean	EC, K, Na, Ca, Mg, Cu, Zn, Mn, Cl, NO <sub>3</sub> , Br, organic matters	Lab scale	Japan	Nishikawa et al., 2007

## **1.2 Research flow**

This study is mainly consist of four parts. Fig. 1.3 explains the basic concept behind the flow of this research and the future perspectives. As shown there, a water quality monitoring session was conducted at a selected open solid waste dumpsite in Sri Lanka. Evaluation of the current contaminant levels is essential to identify the most critical contaminants. Further it is necessary to evaluate their temporal variation. The contaminant concentration may vary with different factors as mentioned in the introduction. Hence, the PRBs should have capacity to treat the polluted water even the contaminant flow reached their highest contamination level (fig. 1.3). Furthermore, this is important in planning and designing of the numerical modeling of groundwater contamination and other rehabilitation technologies. As the second step of the research, a numerical simulation was conducted to observe the potential future risk of groundwater contamination and the effectiveness of a virtual PRB set at the downstream of the open solid waste dumpsite. The conceptual contaminated site was classified based on data collected from the data collected from part 01 of the study. In the simulation, the virtual PRB was assumed to be a mixture of soil a biochar, the input parameters for the adsorption properties of this mixture was referred (Paranavithana et al., 2016). The limitations were found there as the nonappearance of the effect of the environmental factors on the adsorption (pH, ionic strength), desorption and competitive adsorption properties, and hydraulic properties of the virtual PRB etc. Since, a critical evaluation of those properties of the selected PRB materials were highly demanded, the laboratory experiments were conducted to achieve those targets by conducting batch and column studies in 3rd and 4th steps of the research. There, the best mixing proportion of the PRB filling material was determined among tested adsorbents, based on the adsorption, desorption, hydraulic properties and long-term performances. As the next step, researchers should move to the field experiments which

represent the actual scenario of the contamination.

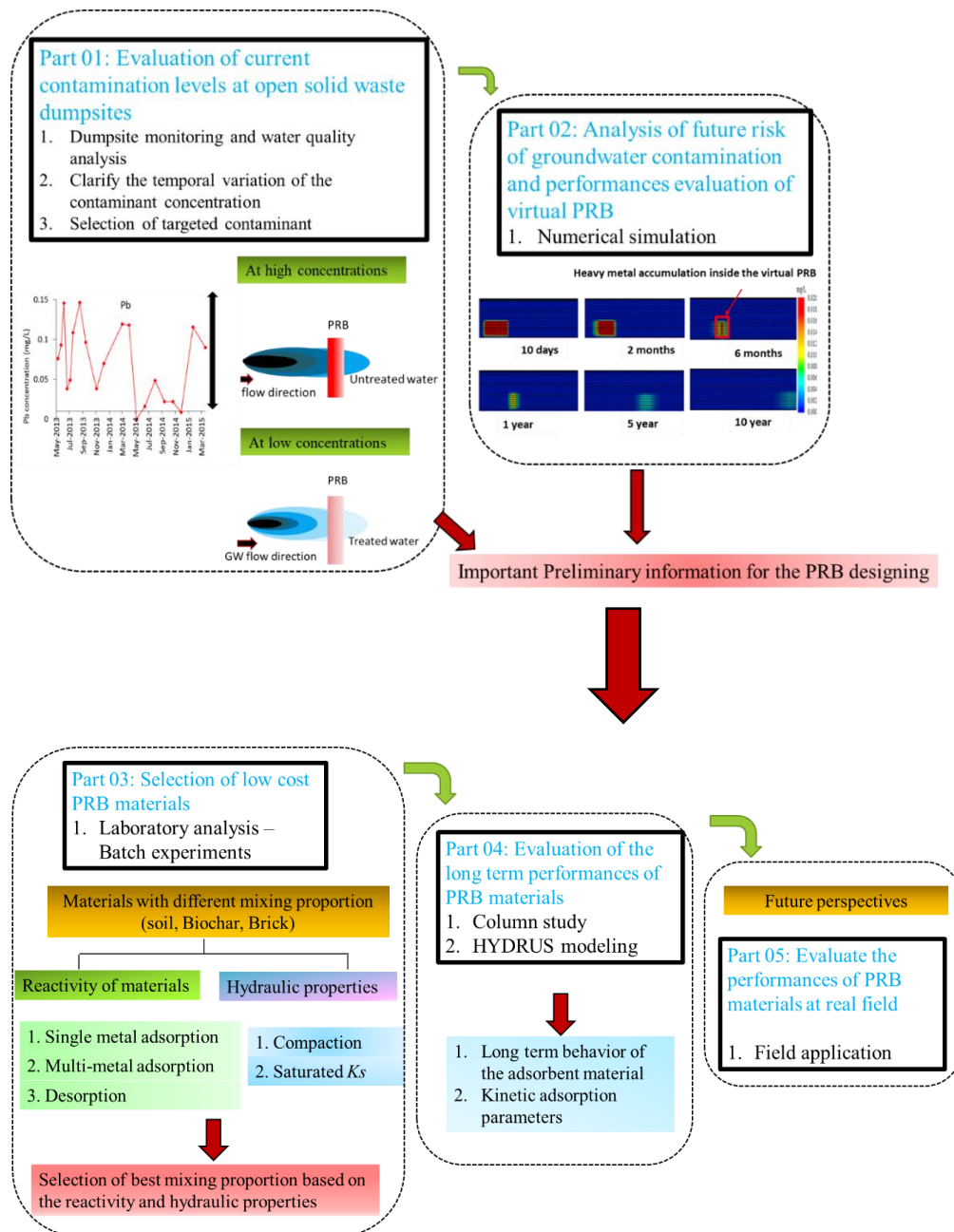


Figure 1-3 The basic concept of the research flow

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## **Chapter 02. TEMPORAL VARIATIONS IN PERCHED WATER AND GROUNDWATER QUALITIES AT AN OPEN SOLID WASTE DUMPSITE IN SRI LANKA**

### **Abstract**

The common waste disposal method of municipal solid waste in developing countries is the dispose in to open dumpsites. The waste is dumped into the open sites without any preliminary sorting or any other pretreatment. The open dumpsites are basically selected without any environmental impact assessment, but based on the easiness of the waste transport into the sites and land availability. Commonly, river banks and marshy lands selects as the final waste disposal sites while treating the ecosystem into a severe pollution. The landfill leachate generates as a product of waste degradation may contain high concentrations of organic matter, inorganic matter, xenobiotic compounds and heavy metals. Once the leachate mixed into the water bodies, creates severe damages on the ecosystem. Thus the identification of the level of severity is essential to follow up the required treatment facilities and pollution remediation technologies. In this study, a long-term monitoring session was conducted at an open solid waste dumpsite from March 2013 to March 2015 and the water quality was observed for their organic, inorganic and heavy metal contaminants. The selected study area was an abundant open solid waste dumpsite located in Udapalatha PS, Central Province, Sri Lanka, and at a sloppy bank of a Mahaweli river. The dumpsite has two sections namely Old section and New section based on the age of the usage. The old section has been used for 7 (2003-2010) years of dumping and the new section was used only for 6 months (2011) of dumping. The perched water monitoring boreholes and groundwater monitoring boreholes were installed at the both sections, additionally one groundwater monitoring borehole was installed at intact area to the dumpsite. The monitoring session was conducted once a month, both perched water,

groundwater and surface water from a nearby river were collected and analyzed for water quality parameters such as pH, EC, BOD, COD, TN, TP, major cations, anions, and heavy metals. Weather data such as rainfall were collected from a nearby rain gauge station. There is a slight negative correlation was observed between rainfall and perched water quality. Further, there was significant linear correlation between EC and major equivalent cations/anions, suggesting EC is a simple and convenient parameter to characterize the dumped waste condition. A well-recognized tool, Leachate Pollution Index (LPI) was used to characterize the level of contamination, for better capturing of the temporal variation of the water quality. The results shows that the groundwater samples from both Old and New sections had lesser contamination levels than the perched water. This seems to be the presence of the two independent water bodies in the dumpsite as the local perched water aquifers and groundwater aquifers in both Old and New sections. The perched water from new section had high contamination levels than the old section, can be suggested as the washing out or the deep penetration of the waste contaminants generated in the old section. In this regard, the implementation of the treatment facility is highly demanded to avoid mixing of leachate with the groundwater and surface water bodies.

## **2.1 Introduction**

Landfills are one type of ordinary method of waste disposal, many parts of the world still practicing (Meththika et al; 2014). Uncontrolled dumping of Municipal Solid Wastes (MSW) is practice in three-fourths of countries in the world even though it creates a number of problems to the environment (Ariyawansha et al., 2010). Especially in developing countries in tropical areas of the world, open dumping is used very often, while creating many issues. According to Trankler et al; (2005) more than 90 % of all landfills in South and Southeast Asia are non-engineered including Sri Lanka. Open dumps in most of the tropical regions fill with Municipal Solid Wastes (MSW) commonly known as trash

garbage which containing household domestic waste, industrial wastes with the exception of industrial hazardous wastes (Meththika et al., 2014).

Open dumpsites are not designed lands for waste dumping; there are no landfill liners, leachate collection systems, final soil covers or leachate treatment mechanisms. For the establishment of a landfill, the basic requirement is the availability of any vacant land with government ownership but no environmental guidelines are considered and This type of dumpsites requires minimum operational and maintenance costs (Meththika et al; 2014). Most of the time land closer to the natural water bodies and sloppy areas are the susceptible places due to the easy disposal of waste. The wastes are openly dumped on the top soils and continuous the usage even after reached their maximum bearing capacities. Even though the open dumping of waste is cheaper than other waste treatment practices, it creates a number of socio-economic and environmental issues. These landfills are susceptible to open burning, spread the diseases, skin diseases caused by garbage and dumps (Joseph et al; 2002) and create social impacts such as breeding of mosquito, loss of property of surrounding lands, bad odour. The environmental impact caused by landfills is critical, it contaminates air, soils, groundwater and surrounding water bodies from generated toxic materials (Vidanaarachchi et al., 2006).

Commonly, no waste segregation is practicing before it is dumped into the sites, thus the composition of the waste is highly heterogeneous. This may lead to severe environmental impacts, especially the surface and groundwater contamination is predominant at open solid waste dumpsites.

Many groundwater contamination incidents have been reported at open dumpsites and their surroundings, caused by leachate. The landfill leachates generate as a result of waste degradation which contains or entrained environmentally harmful substances. It is a very

concentrated solution having higher levels of Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Electrical Conductivity (Christensen et al., 1998). Leachate is a dark color solution, which generated from decomposition of waste in the dump site. The density of leachate is also higher than water it is around 1.14 kg/L at 10 °C due to the presence of huge loading of salts. Leachate consists of different organic matter such as humic acid, fulvic acid and inorganic compounds that may be either dissolved or suspended (Hamidi et al., 2014). Heavy metals may release by waste such as ceramics, electronic wastes, batteries, debris of motor mechanic industry etc. High concentrations of Cd, Hg, Ni, Mn, Cu, and Pb have been reported from leachate collected at many open dumpsites (Chen., 1996).

There are main three water sources for the leachate, as water coming from rainfall, water coming out from the waste material due to its metabolic reactions, water squeezed out from the waste materials due to upper loading. Municipal solid waste, such as kitchen garbage has comparatively higher moisture contents than the other waste materials. Therefore the production of leachate is much higher (Christensen et al., 1998). Leachate generated at waste layers and rainwater drains downward by gravitational forces, stagnated at the bottom of the waste dump. This polluted water enters to groundwater aquifers through the soil. The subsequent migration of leachate through the sides and/or bottom of the dumpsite into subsurface formations is a serious environmental pollution concern and it is a threat to public health and safety. In this context, groundwater pollution is by far the most significant concern arising from leachate migration. The level of contamination mostly depends on the severity of leachate quality at open dumpsites.

Quality of leachate greatly varies with respect to the type of waste, the age of the dumpsite, management practices at the dumpsites, climatic factors and etc. Age of the dumpsite has a significant influence on the quality of leachate since the phase changes of landfill occur



with the age. This phase changes of waste degradation are due to the changes in microbial activities and the variations of the Oxygen availability enclosed by the waste layers. Biological degradation occurs with the natural presence of bacteria. The tropical climates create a favorable environment for the microbial activities encouraged by high temperature and adequate amounts of rainfall thus lead rapid degradation of waste (Irene 1996).

There are main four phase changes can be observed in the landfill leachate as, aerobic phase, anoxic – nonmethanogenic phase, anaerobic- methanogenic unsteady phase and anaerobic- methanogenic steady phase.

In the early stage, decomposition of waste in landfill layers occurs under aerobic conditions since oxygen is still present between the compacted waste layers. However, this condition only last for few days or weeks. This aerobic decomposition produces heat as high as 80-90 °C and a complex solution with neutral pH value. This stage does not much contribute to leachate generation but generated high temperature important to the further decomposition of wastes (Edward et al., 1995).

The activity of the anaerobic and facultative organisms is enhanced at the second phase of the waste degradation, once the oxygen has been fully utilized. Hydrolyze and ferment cellulose and other putrescible materials result simpler soluble compounds such as volatile fatty acids and alcohols may cause high biological oxygen demand (BOD) in tropical leachate which is called as “acetogenic leachate.” According to Christensen et al., (2001) acetogenic leachate is characterized by acidic pH, high BOD/chemical oxidation demand (COD) ratio, high concentrations of ammonium nitrogen ( $\text{NH}_4^+ - \text{N}$ ), and strong unpleasant smells. Volatile fatty acids are the predominant contaminant presents in the dissolved organic carbon (DOC) found in acetogenic leachate and it is > 95% of the total (Harmsen, 1983). Acetogenic leachate also rich with volatile amines and alcohols and this

may be the reason for acidic pH (Shuokr et al. 2010). In addition, inorganic ions such as sulfate, calcium, chloride, and magnesium also present in the leachate generated in this stage.

After several years of acetogenic phase, methanogenic phase arrives, while facilitating activities of methanogenic bacteria to release simple organic compound from the available complex organic compounds. Methanogenic leachate has alkaline pH, lesser BOD and COD levels whereas the higher levels in acetogenic leachate (Shuokr et al. 2010). Methanogenic leachate 32 % of DOC consists of high-molecular-weight compounds (MW > 1,000), such as humic and fulvic acids, which are not easily degradable and may contribute to the high COD (Christensen et al. 2001). In addition to organic compounds inorganic ions such as sulfate, nitrate, are lower due to the reduction processes. No volatile compounds found in methanogenic leachate, whereas presence of ammonia predominant. This stabilized leachate may have the ability to persist for several decades. Apart from the age of the dumping, there are several other factors such as rainfall affects the leachate quality.

Rainfall is the means by which outside water infiltrates the landfill system and causes the increase of the amount of leachate generation. Even though there is a quantity incensement of leachate with the rainfall, it also changes the concentration of leachate through dilution process (Barber et al., 1994).

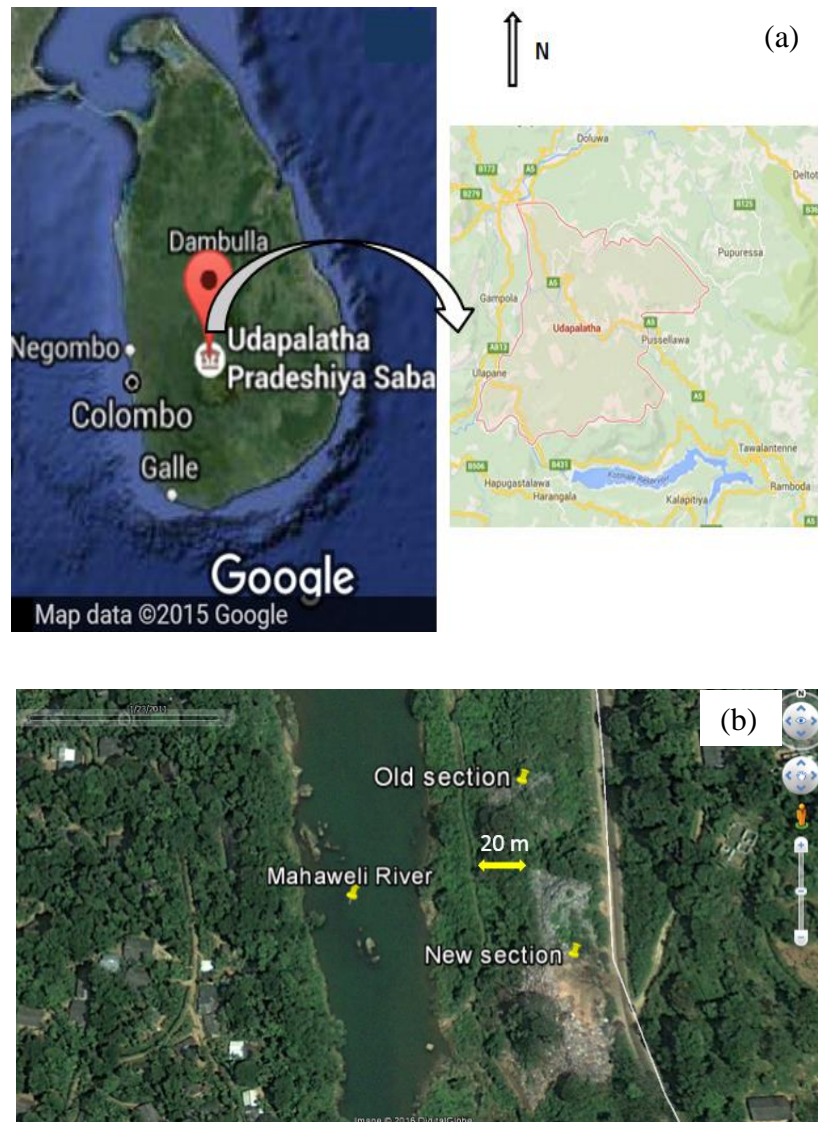
Further the site characteristics such as the slope of the dumpsite and type of the topsoil layer directly affect the leachate quality as well as the degree of the groundwater contamination. Steep slope encourages the rapid washing out of the contaminants with the precipitation and the level of infiltration determines by the soil mineralogy.

As the several factors affect the leachate quality, it varies greatly, yet the leachate quality characterization is highly important to suggest the treatment facilities to minimize the environmental impact (Christensen et al., 2001). Leachate Pollution Index (LPI) is an internationally used tool which developed for the leachate characterization with respect to the vulnerability and severity of contamination. LPI quantitatively analyze the severity of organic pollutants, inorganic pollutants and heavy metals with the different sub-indices of LPI (Umar et al., 2010). LPI varies between 5-100, which the smallest value represents the lower pollution potential whereas the increasing LPI reflects the higher potential in environmental pollution. This might be successfully used for the implementation of leachate treatment mechanisms and identification of groundwater pollution potential at open dumpsites. This study is a focused assessment of water quality and its variability using LPI indices and identification of different categories of perched water and groundwater in the same dump site.

## **2.2 Materials and Methods**

### **2.2.1 Site selection**

Fig. 2.1 (a) shows the location of the dumpsite in Sri Lanka and fig. 2.1 (b) shows the google image of the dumpsite. The monitored dumpsite belongs to Udapalatha PS, Central province, Sri Lanka Sabha ( $07^{\circ} 80' 30.1''$  N and  $80^{\circ} 34' 43.2''$  E) and the average annual rainfall is above 2000mm with an average annual temperature of  $24.7^{\circ}\text{C}$  (Census and Statistics. 2010). The waste dumping rate was approximate, 15-20 ton/day at the time of operation. The dumpsite has been abandoned at the time of the monitoring session. and consists of distinguishable sections;



boreholes were installed up to original soil layer. Fig. 2.2 (a) shows the bore hole location in the dumpsite and fig. 2.2 (b) shows the cross sectional view of the dumpsites.

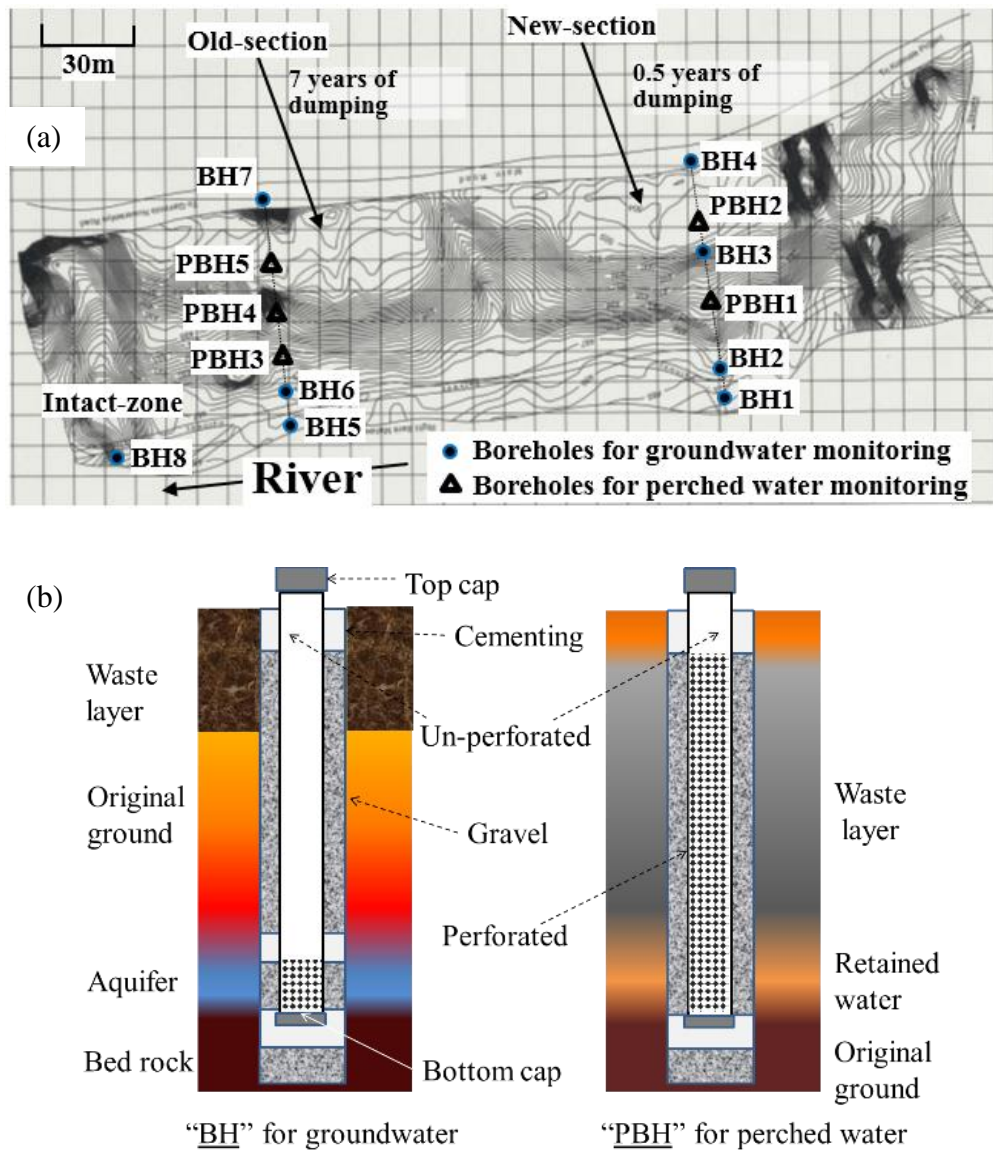


Figure 2-2 (a) Location of the boreholes at the dumpsite and (b) the cross sectional view of the boreholes.

### 2.2.3 Monitoring water quality

The dumpsite was monitored for two years of the period from May 2013 to March 2015 with one-month interval. Perched water samples were collected from PBH wells, groundwater samples were collected from BH wells, and surface water collected from river

Mahaweli. First, pumped out the well water by manual pulping, to facilitate freshwater sampling and the water samples were collected into clean 1L polypropylene bottles. Water samples were analyzed into main water quality parameters such as BOD, COD, TOC, Major cations/anions, and heavy metals. Onsite parameters were taken for pH, EC, water temperature. Standards methods were used to analyze BOD<sub>5</sub> (APHA 5210B) and COD (APHA 5220A). TOC analyzer (TOC-LCSH/TNM-L Shimadzu, Japan) was used to measure the TOC and TN. Anions; Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> were analyzed with ion chromatograph (HPLC-IC, SHIM-PACK IC-A3 Shimadzu, Japan). Cations; Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> were analyzed with atomic absorption spectrophotometer (7000 Shimadzu Corporation, Japan) and NH<sub>4</sub><sup>+</sup> was analyzed with UV-Vis Spectrophotometer (UV-2700 Shimadzu, Japan). Heavy metals; Fe, Ni, Cu, Zn, Pb were measured with AAS and As, Cr were analyzed with Inductively coupled plasma mass spectrometry (ICPM-8500, Shimadzu, Japan).

Rainfall data were collected from a close by a rain-gauge station to the dumpsite.

#### 2.2.4 Leachate pollution index

The temporal variability of the water quality was analyzed with *LPI*. Sub-indices of *LPI*; *LPI* organic, *LPI* inorganic and *LPI* heavy metals were calculated according to the equation 2.1 (Esakku et al., 2003). Then the overall *LPI* was calculated by equation 2.2.

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

$$LPI_{\text{overall}} = 0.232 LPI_{\text{or}} + 0.257 LPI_{\text{in}} + 0.511 LPI_{\text{hm}} \quad (2)$$

where *LPI* is the leachate pollution index,  $w_i$  is the weight for the  $i^{\text{th}}$  pollutant variable,  $p_i$  is the sub-index score of the  $i^{\text{th}}$  pollutant variable and, n is the number of leachate pollutant variables used in calculating *LPI* (Esakku et al., 2003; Kumar and Alappat 2005a).

After analyzing the water samples for different water quality parameters sub-index values were calculated according to the weight factors (Esakku et al., 2003). Finally, the overall *LPI* was calculated. The perched water and groundwater quality were compared with the *LPI* calculated for effluent water quality standards of Sri Lanka. Table 2.1 shows the *LPI* calculation for the study area.

## **2.3 Results and Discussions**

### **2.3.1 The temporal variation of the water quality**

Fig. 2.3 exemplify the temporal variation of general water quality parameters. Organic contaminants, inorganic contaminants, heavy metals, and *LPI* indices, in both Old section and New section of the dumpsite and those, were compared with the rainfall and water temperature. Temporal variability of perched water quality at new section was evaluated by observing PBH2 whereas PBH4 was used for the old section. BH2 and BH6 respectively used to evaluate groundwater quality variations at new and old sections.

Perched water consisted of high contamination levels than the groundwater throughout monitoring session. All the water quality parameters observed in perched water collected from the New section of the dumpsite was always higher than the Old section. The BOD, COD, TN, TP of the perched water at New sections of the dumpsite fluctuated at high concentrations. Even though TN at Old section was lower than the New section, always exceeded the WHO drinking water quality standards (WHO, 2011). EC of the perched water at new section showed high values; it is higher than 10 times that of perched water at old section and groundwater at both sections. This reveals the presence of high ionic concentration at the perched water at New section and reduction of inorganic ions in leachate with the age of the dumping. Heavy metals (Cr, Pb) and pH of the both perched and groundwater samples showed similar, low values. The BOD and COD of perched

water were always lower than the Sri Lankan drinking water quality standards (CEA, 2011).

The  $LPI_{in}$ ,  $LPI_{or}$  and  $LPI_{overall}$  calculated for PBH2 are 3 - 4 times higher than perched water and groundwater samples analyzed at other wells. Perched water well at old section; PBH4 showed comparatively higher values than the groundwater in old section at the initial stage of the monitoring session.  $LPI$  indices calculated for both Old and New sections reduced with the time as the reduction of the level of contamination due to the washing out or leaching of contaminants with the time. The contaminants might dissolve in the rainwater and move towards the river due to the steep slope of the site. Minor contamination of groundwater aquifer reveals that effect of infiltration is lesser than the effect of runoff on this site.

### **2.3.2 Effect of age of the dumpsite on leachate quality**

As described in the introduction the quality of the leachate depends on the different physiological processors happens at dumped wastes, which is corresponding to the age of the dumping Fig. 2.4a shows the 1:1 plot developed for the  $LPI_{overall}$  at PBH2 vs. PBH1 (New section) and at PBH4 vs. PBH3 (Old section). The  $LPI_{overall}$  at new section varies greatly, than at the new section, the contamination level has been reduced with the aging. The  $LPI_{overall}$  calculated in both upslope and downslope of the new section is varies within the range of 5-20, whereas in old section it is only scattered around 5. This might be due to rapid degradation of waste, dissolution and attenuation of the contaminants over the time. Same results were observed in Malaysia, which is a comparative study to differentiate  $LPI_{overall}$  over the aging effect. It is found that the  $LPI_{overall}$  calculated for old dumpsites are comparatively lower than that of new dumpsites (Muhammad et al., 2010). Fig. 2.4b exemplify the effect of age of the dumpsite on leachate quality. The  $LPI_{overall}$  at



PBH2 was plotted in a 1:1 plot against the *LPI<sub>overall</sub>* at PBH4. The same plot was developed to compare the groundwater (BH2 Vs BH6). The variation in leachate quality (*LPI<sub>overall</sub>*) observed at PBH4 is narrow compared to PBH2 showing that the sensitivity of new waste than old waste. Further, the level of groundwater contamination is very low both in new and old sections. There was no fluctuation of *LPI<sub>overall</sub>* observed in groundwater, reveals that the independency of the groundwater aquifer from the perched water. This might be due to the steep slope (15m/50m) of the dumpsite and the different permeabilities

Table 2-1 Sub-indices and LPI overall calculated for PBH2, BH for June 2013 and effluent water quality (Sri Lanka)

Index	Parameter	New section : Perched water (PBH2)					New section : Groundwater (BH2)					Effluent water quality standards				
		Value*	Sub-index	Weight factor	WiP <sub>i</sub>	LPI	Value mg/L	Sub-index	Weight factor	WiP <sub>i</sub>	LPI	Value mg/L	Sub-index	Weight factor	WiP <sub>i</sub>	LPI
LPI <sub>or</sub>	BOD	11.0	5.02	0.061	1.3	9.3	6.40	5.00	0.263	1.3	6.1	30	5.4	0.061	1.4	7.7
	COD	333	13.5	0.062	3.6		115	7.18	0.267	1.9		250	10.0	0.062	2.7	
LPI <sub>in</sub>	pH	7.10	5.00	0.055	1.0		6.40	5.00	0.214	1.0		6-8.5	5.0	0.055	1.1	
										7						
	TDS (E03)	3.20	9.00	0.05	1.8	17	0.93	6.10	0.195	1.2	5.9	1.75	7.2	0.05	1.4	6.3
	TN	856	27.2	0.053	5.6		146	7.09	0.206	1.4		150	7.1	0.053	1.5	
	NH <sub>4</sub> <sup>+</sup> -N	472	41.5	0.051	8.2		98.6	9.90	0.198	1.9		50	7.1	0.051	1.4	
	Cl <sup>-</sup>	331	6.18	0.048	1.2		272	5.97	0.187	1.1		1	5.0	0.048	0.9	
LPI <sub>hm</sub>	Total Fe	7.60	5.20	0.045	0.5		10.0	5.25	0.088	0.5		3	5.1	0.045	0.4	
	Cu	0.01	5.01	0.05	0.5		0.001	5.00	0.098	0.5		3	20.0	0.05	2.0	
	Zn	0.20	5.04	0.056	0.6		0.06	5.01	0.110	0.6		2	5.4	0.056	0.6	
	Pb	0.03	5.15	0.063	0.6		0.07	5.28	0.123	0.6		0.1	5.4	0.063	0.7	
	Ni	0.06	5.14	0.052	0.5	5.1	0.04	5.09	0.102	0.5	5.1	3	10.0	0.052	1.0	7.8
	As	0.01	5.01	0.061	0.6		0.002	5.01	0.119	0.6		0.2	5.4	0.061	0.6	
	Cr	0.04	5.09	0.064	0.6		0.05	5.11	0.125	0.6		0.1	5.2	0.064	0.7	
LPI <sub>overall</sub>		9.3							5.7							6.1

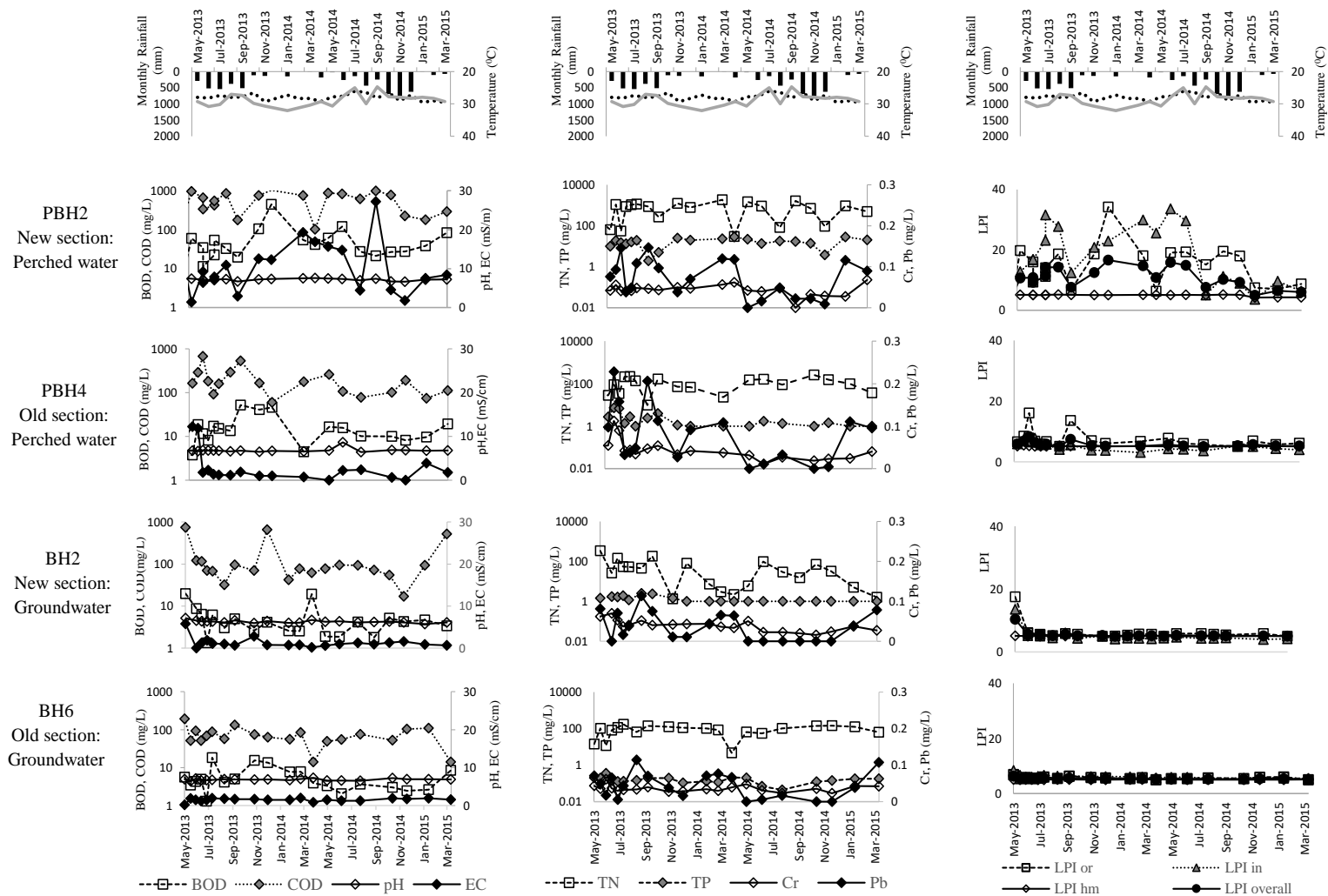


Figure 2-3 Temporal variability of meteorological parameters, water quality variables, and leachate pollution indices of monitoring boreholes

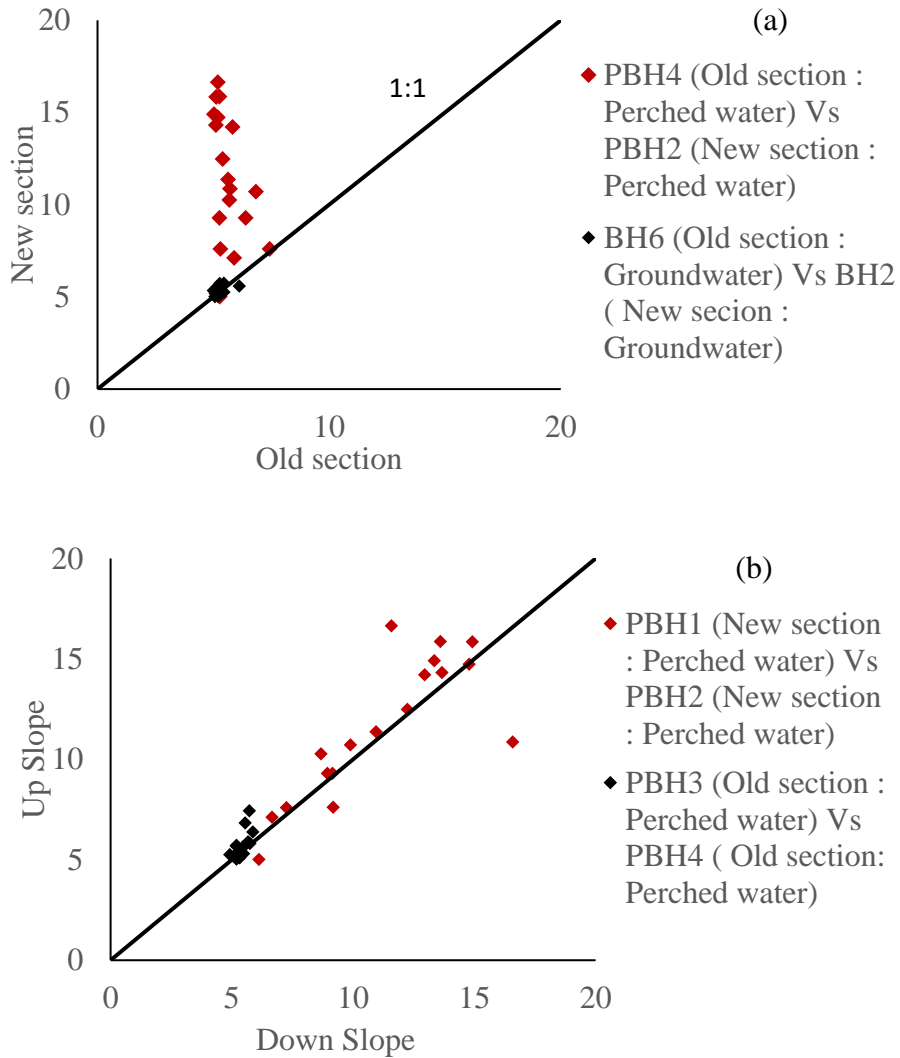


Figure 2-4 1:1 Relationship between LPI overall in monitoring boreholes

of the waste and soil layers. Lower permeability of the soil may facilitate the development of the perched water aquifer between original soil layers and buried wastes. Thus the groundwater contamination at this dumpsite is comparatively lower. Similar phenomena were observed by (Esakku et al.,

2003), that development of a perched water aquifer in an open dumpsite in Chennai, India.

### **2.3.3 Effect of climatic factors on leachate quality**

The effect of rainfall on water quality parameters was analyzed separately for the perched water and groundwater. A general trend was observed between each mentioned perched water quality parameter and monthly rainfall and it is illustrated in fig. 2.5a. BOD, EC, LPI overall, Pb concentration has a reducing trend with increasing rainfall amount. The dilution of contaminants can occur with the high rainfall. Similar trends were observed at Gohagoda dumpsite at the same district of the study area (Wimalasuriya. et al., 2011). There is no any correlation or general trend observed in groundwater quality parameters and rainfall (fig 2.5b). The reason might be due to the independence of groundwater aquifer from the perched water aquifer in this site. Thus the site hydrology is an important factor that governs the leachate and groundwater quality in open dumpsites.

### **2.3.4 Interrelationship between leachate quality and EC**

Figure 2.6: (a) Major Equivalent cations Vs EC and (b) Major Equivalent anions Vs EC.

Figure 2.6 (a) and (b) show the relationship developed for EC and major equivalent cations, anions observed in perched water monitoring wells.

Major cations found in perched water are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and major anion is  $\text{Cl}^-$ . A similar result was found by a previous research which has been done for the leachate quality analysis in Sri Lanka (Sewwandi et al., 2013). The presence of higher loadings of unsorted municipal solid wastes in landfills may govern the easy release of the major cations and anions into the leachate. Further  $\text{Cl}^-$  is highly mobile under all conditions. Thus it is a readily available ion and directly contribute to the EC.

As shown in fig. 2.6 both major equivalent cations and anions calculated for perched water, collected from both new and old sections highly correlate with the EC. The regression coefficients of the correlation were also given in the figures and show a strong positive correlation for both cations vs. EC and anions vs. EC as of 0.79 and 0.77 respectively.

For the calculation of major anion  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  were used and the rest of the effect might contribute by organic anions which are not considered here. The source of this  $\text{HCO}_3^-$  might be degraded solid waste or the rainwater. Further this  $\text{HCO}_3^-$  might not come with the geomorphological characters of the site, since the pH of the water is around neutral values (Dergisi et al., 2010).

The concentration of major equivalent cations is notably higher than that of major equivalent anions. Since the leachate is rich in organic anions such as Acetate, propionate, butyrate, anions of fatty acids, amino acids and other anion compounds, the contribution for the major equivalent.

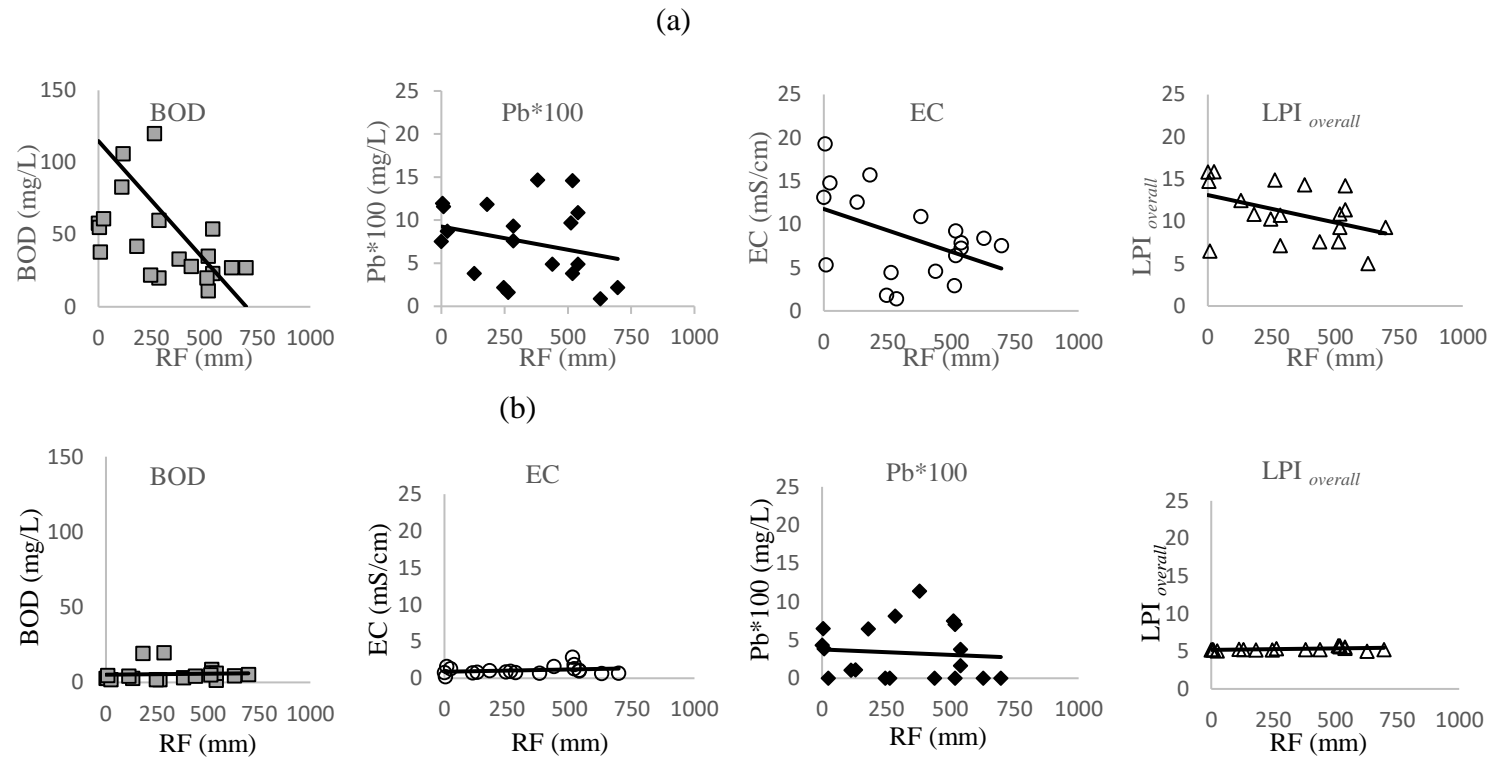


Figure 2-5 Rainfall Vs Major parameters of (a) PBH2 (Perched water : New section) and (b) BH2 (Groundwater : New section)



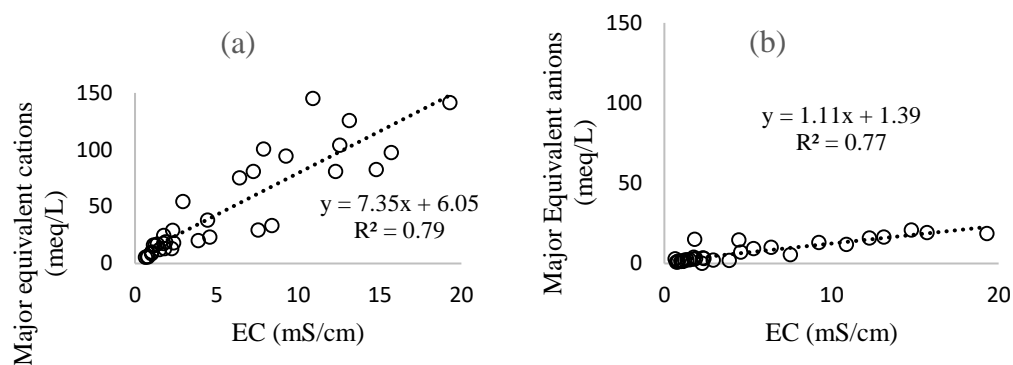


Figure 2-6 Major equivalent cations vs. EC (a) and major equivalent anions vs. EC of perched water

anions might mainly govern by organic anions (Christensen et al., 2000). A study conducted in a landfill in Jordan and they found that 11% of total alkalinity is covered by low molecular weight organic acids in collected leachate. Further, as detected by total organic carbon fraction analysis, it found that 52% of total alkalinity contribute by organic anions in the leachate (Baedecker and Back., 1979). Thus the organic anion is a major factor that contributes to the total equivalent anions in leachate.

However, the correlation between major equivalent cations, anions with EC conductivity is more than 0.75 as found here, concentrations of major equivalent cations and anions might describe by EC, which is an easy and portable measurement at the field level.

## 2.4 Conclusions

Major water quality parameters and  $LPI_{overall}$  calculated for perched water generated at the New section of the dumpsite is higher than perched water at old section and groundwater. The contamination level decrease with time even in the perched water generated at the New section with the time. High temperature and rainfall might govern the rapid degradation of waste and dissolution, thus landfill stabilization is rapid in tropical countries rather temperate countries. Further age of the dumpsite is a major factor that governs the landfill leachate quality.

Groundwater aquifer and local perched water aquifer persist as two different water bodies, in this particular dumpsite. Thus the groundwater contamination is less. The low permeability of the dumpsite might facilitate stagnate leachate at the waste profile and bottom of the waste layers, than infiltration through the soil. Hydrology of the dumpsites has a great effect on the level of groundwater contamination at open solid waste dumpsites.

Water quality parameters and rainfall have a slight negative correlation. Increased rainfall level made the reducing trend of contaminant concentrations. High rainfall levels might facilitate the dissolution and rapid runoff of contaminants at the dumpsite.

There were significant linear correlations between EC and major equivalent cations/anions, suggesting EC is a simple and convenient parameter to characterize the leachate and dumped waste conditions.

The contribution of organic anions on total equivalent anions should be high in leachate. Thus organic anions should include, when calculating total equivalent anions, in leachate *LPI* is an effective tool to characterize the leachate and select suitable treatment facility for the different groups of the leachate.

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# **Chapter 03. SIMULATION OF TWO-DIMENSIONAL HEAVY METAL TRANSPORT IN AN AQUIFER AT SOLID WASTE DUMPSITE: ESTIMATING THE EFFECTIVENESS OF A PERMEABLE REACTIVE BARRIER ON HEAVY METAL POLLUTION CONTROL**

## **Abstract**

Open dumping of solid waste causes serious environmental risk of surface and groundwater contamination due to landfill leachate rich in heavy metals. The severity of the heavy metal contamination has been identified by the several studies and most of the leachate collected from the dumpsites exceeded the maximum permissible levels of effluent water quality standards. The remediation methods are important to minimize the contamination of the water bodies surrounded by the open solid waste dumpsites. Identification of contaminant flow and implementation of remediation technologies including permeable reactive barrier (PRB) are highly demanded in developing countries. In this case study, Geo-Environmental Risk Assessment System (GERAS) has been used to simulate two-dimensional heavy metal transport in an aquifer at solid waste dumpsite and to estimate the effectiveness of PRB on trap heavy metals. In the simulation, the targeted heavy metals were set to be Pb and Cd based on the results of water quality analyses at an abundant solid waste dumping site in Sri Lanka. Two scenarios were examined: 1. An open dumping of waste (pollutant source) located above the aquifer (direct intrusion of rainfall through waste layer) and 2. A buried dumped waste inside the aquifer (no intrusion of rainfall). Concentration changes of heavy metals inside the aquifer beneath the waste later, upstream to PRB, inside the PRB and downstream points were monitored by changing the hydraulic gradient and pollution load. Next, a virtual PRB was

set in downstream of the aquifer by installing a section with a high heavy metal adsorption capacity (based on previous studies). The numerical simulations well captured the wash-out process of heavy metals from the pollutant source and the time period needed to have of full wash-out was highly dependent on the hydraulic gradient, pollution load, distribution coefficient and the way of waste dumping. Results showed that the virtual PRB trapped the target metals and the downstream heavy metal concentrations were reduced less than the effluent water quality standards.

### **3.1 Introduction**

### **3.2 Materials and Methods**

Open dumping is the most common method practice for the final disposal of municipal solid waste in most developing countries (Christensen et al., 2001). The landfill leachate is rich in toxic heavy metals and this causes serious soil and groundwater pollution once it permeates through the original soil layers and aquifers (Udayagee et al., 2017). Thus, identification and mitigation of groundwater contamination by heavy metals at open solid waste dumpsites have been highly important. The Permeable Reactive Barrier (PRB) system, an in-situ method used for treating contaminated groundwater is tested recently by several researchers. The PRB is able to trap and immobilize the heavy metal inside the system (Park et al., 2002); thus become an option to remediate contaminated groundwater plums at the open solid waste dumpsites. PRB system does not interrupt the groundwater flow in the treatment process and take advantage of the passive flow of the groundwater, thus highly suitable to use as in-situ pollutant immobilization technique in a cost-effective way. In this study, a numerical simulation software, Geo-Environmental Risk Assessment System (GERAS) (AIST., 2006), was used to simulate a two-dimensional groundwater flow coupled with heavy metal transport. The effectiveness of PRB on the heavy metals



(Cd and Pb) trap in an aquifer was simulated at the different dumping conditions and site characteristics.

### 3.2.1 Selection of Modeling Area

A conceptual contaminated site was classified based on a previous study (Udayagee et al., 2017). The input parameters used for the simulations were collected from the same dumpsite in the previous study; located in the Central province of Sri Lanka. The dumpsite has been used for 7 years of waste dumping. Fig. 3.1 illustrates the arrangement and settings of the conceptual open solid waste dumpsite model. The conceptual open solid waste dumpsite (waste unit) was fixed as 100m in length and 40m in width and the area of the aquifer was set to be 400m x 100m in x and y-direction. The thicknesses of the aquifer and waste unit were set to be 2m. A 4m width and 45m length virtual PRB was installed in the downstream (20 m away from the end point of the dumped waste in the x-direction). In the simulations, two cases were studied: Case 1: Direct open dumping of waste;

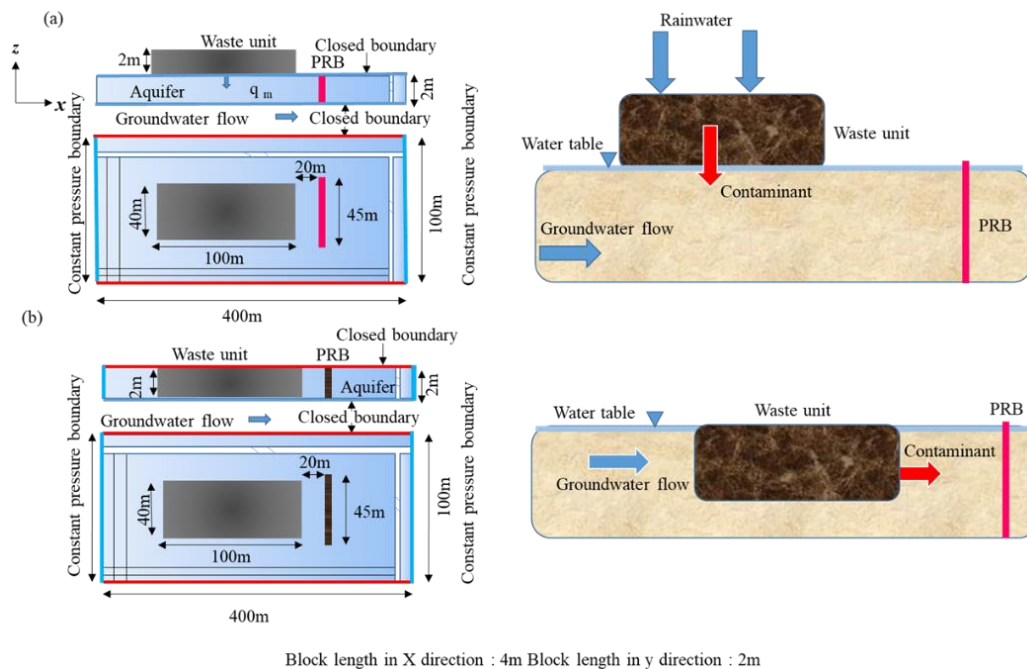


Figure 3-1 Scale and initial boundaries of conceptual model for simulation: Case 1 [a] and Case 2 [b]

the pollutant source is located above the aquifer and direct permeation of rainwater into the aquifer through the waste layer (Fig. 3.1a). Case 2: A buried waste dump inside the aquifer, no effect of rainfall, groundwater flow affects the washing out of contaminants (Fig. 3.1b). Spatial and temporal variability of contaminants and the effectiveness of the PRB were evaluated in both cases by analyzing the changes in heavy metal concentrations at upstream, downstream and inside the PRB.

### 3.2.2 Governing Equations

GERAS simulation model is used to estimate contaminant concentration (heavy metals) in the groundwater as a function of time and space. The model simulation is considered to be two dimensional in the horizontal plane. The model uses partial differential equations and set of auxiliary boundary conditions for the simulations and the governing equations have applied for three main zones at the contaminated sites.

#### 3.2.2.1 Zone 1: Aquifer

The model follows the flow equations as shown in Eqs. (3.1) and (3.2). The model assumes three assumptions in the application of these equations as

1. Water is an incompressible fluid
2. Fluid pressure created by groundwater is low
3. Aquifer is homogeneous, and isotropic porous media (Bear 1972).

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0 \quad (3.1)$$

$$v_x = \frac{-k_x}{n_a} \cdot \frac{\partial \phi}{\partial x} \text{ and } v_y = \frac{-k_y}{n_a} \cdot \frac{\partial \phi}{\partial y} \quad (3.2)$$

where  $\phi$  [L] is the pressure head,  $v_x$  and  $v_y$  [ $\text{LT}^{-1}$ ] are the groundwater velocities in  $x$  and  $y$  directions,  $k_x$  and  $k_y$  [ $\text{LT}^{-1}$ ] are the hydraulic conductivities in  $x$  and  $y$  directions,  $n_a$  [-] is the porosity of aquifer.

A solute transport equation used in the simulations was as follows:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D_x \frac{\partial C}{\partial x} \right] + \frac{\partial}{\partial y} \left[ D_y \frac{\partial C}{\partial y} \right] - \left[ V_x \frac{\partial C}{\partial x} + V_y \frac{\partial C}{\partial y} \right] - \left[ \frac{1-n_a}{n_a} \right] \rho_s \frac{\partial S}{\partial t} \quad (3.3)$$

where  $C$  [ $\text{ML}^{-3}$ ] is the solute concentration,  $t$  is the time,  $D_x$  and  $D_y$  [ $\text{L}^2\text{T}^{-1}$ ] is the diffusion coefficient in  $x$  and  $y$  directions,  $S$  [ $\text{MM}^{-1}$ ] is the saturated adsorption of contaminant into soil particles. The  $D_x$  and  $D_y$  are as follows:

$$\begin{aligned} D_x &= \varepsilon D_M + \tau_L |V_x| \\ D_y &= \varepsilon D_M + \tau_T |V_y| \end{aligned} \quad (3.4)$$

where  $D_M$  [ $\text{L}^2\text{T}^{-1}$ ] is the molecular diffusion coefficient of metal (Cd and Pb) in free water and  $\varepsilon$  is the tortuosity according to Millington and Quirk model (1961). The longitudinal and transverse dispersivities,  $\tau_L$  and  $\tau_T$  [L], were determined with respect to the scale of aquifer in the simulation and  $\tau_T$  was considered as 0.1 times of  $\tau_L$ . In the aquifer, linear adsorption model was used for the adsorption of heavy metals into solid phase:

$$S_s = k_{d-w} C_w \quad (3.5)$$

where  $k_{d-w}$  [ $\text{L}^3\text{M}^{-1}$ ] is the distribution coefficient of target heavy metal in the aquifer.

### 3.2.2.2 Zone 2: Waste unit

Few assumptions were made when applying the governing equations to waste unit: 1) heavy metal component in solid waste stocked within the waste unit, 2) dissolution/desorption of heavy metal due to rainfall permeation and groundwater flow in Case 1, and only by groundwater flow in Case 2. Saturated adsorption of heavy metals into waste

particles:  $S_{ws}$  [MM<sup>-1</sup>] were determined following linear adsorption model using the distribution coefficient of target heavy metal in the waste unit:  $k_{d-ws}$  [L<sup>3</sup>M<sup>-1</sup>].

$$S_{ws} = k_{d-ws} * C_{ws} \quad (3.7)$$

The concentration of heavy metal component in porous media of waste ( $C_{ws}$ ) [ML<sup>-3</sup>] is considered to be equal to heavy metal concentration of adjacent soil porous.

Inflow flux of heavy metal in Case 1 follows the Eq. (3.8).

$$q_{hm} = Rq_r C_w \quad (3.8)$$

where  $q_{hm}$  [MT<sup>-1</sup>] is the inflow flux,  $R$  is the permeation ratio,  $q_r$  [L<sup>3</sup>T<sup>-1</sup>] is the rainfall intensity, and  $C_w$  [ML<sup>-3</sup>] is the equilibrium concentration of heavy metal in water phase. Inflow of heavy metal in Case 2 is controlled by Eq. (7).

### 3.2.2.3 Zone 3: Permeable Reactive Barrier (PRB)

Langmuir adsorption model was applied to characterize the heavy metal adsorption at PRB in the simulations:

$$\frac{C_{ws}}{S} = \frac{1}{bQ_m} + \frac{C_w}{Q_m} \quad (3.9)$$

where  $S$  is the adsorbent amount of heavy metal into reactive material,  $b$  [L<sup>3</sup>M<sup>-1</sup>] is the Langmuir constant and  $Q_m$  [MM<sup>-1</sup>] is the maximum adsorption capacity (Bulgariu et al., 2012).

### 3.2.3 Setting of Input Parameters

Table 2.1 summarizes parameters used in the simulations fig. 2 illustrates the general framework of the model simulation.

#### 3.2.3.1 Aquifer

The hydraulic gradient was set for the simulation based on groundwater level measured at the studied dumpsite. The model uses the single value for the calculation and it is assumed that the hydraulic gradient is constant throughout the simulation period. The distribution coefficient of heavy metal in water phase  $k_{d-w}$  was determined considering the soil type of studied area. The soil type of the studied dumpsite is Reddish brown latasolic and the distribution coefficient calculated for the same soil type was used (Paranavithana et al., 2013).

#### 3.2.3.2 Waste unit

The initial concentration of heavy metal was set by considering monitored metal concentrations at studied dumpsite (Udayagee et al., 2017). Referred values (Allison et al., 2005) were used for the distribution coefficient of heavy metal in waste. The field values for the *in-situ* dry density and specific gravity of waste were referred;  $\sim 0.6 \text{ kg/m}^3 \sim 2.3$ ) respectively (Udayagee et al., 2017).

#### 3.2.3.3 Permeable reactive barrier (PRB)

The PRB material was selected based on the previous study (Paranavithana et al., 2016). In the simulations, the hydraulic conductivity of PRB is assumed to be equal to the hydraulic conductivity of aquifer. Rainfall data were collected from a rain-gauge station nearby studied dumpsite (Udayagee et al., 2017).

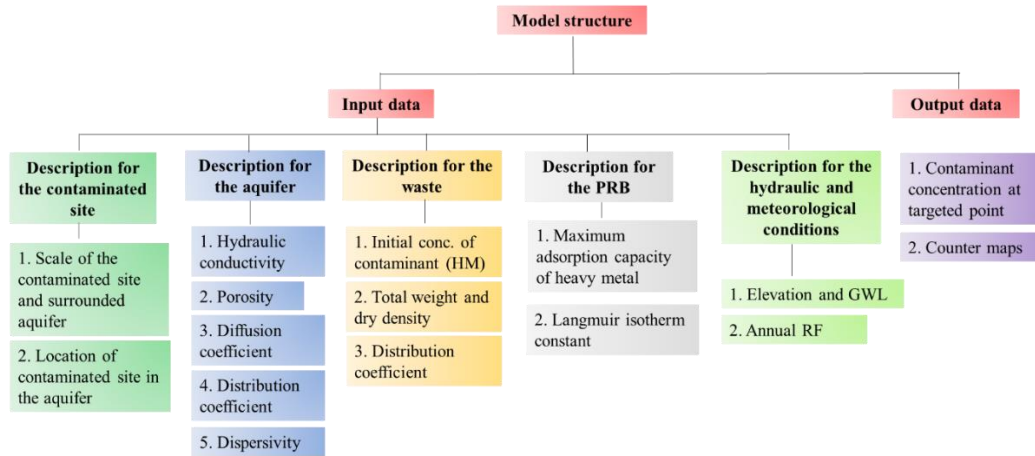


Figure 3-2 General framework of the model simulation

### 3.2.4 Sensitivity Analysis

Sensitivity analysis was conducted to analyze the effect of various input parameters. The values chosen were 1, 0.1, 2 times of the actual input parameter for hydraulic gradient (0.06, 0.006, 0.12). Similarly, the scale of the dumpsite (waste unit) was changed from 100m x 40m to 40 m x 40 m in order to evaluate the effect of pollutant loading. The time taken to reach peak heavy metal concentration in the monitoring points were compared.

The model simulations were also conducted by considering the distribution coefficient of the aquifer  $k_{d-w}$ . The  $k_{d-w}$  for each metal greatly varies with the soil type of the aquifer. According to the Alumaa et al., (2001) the  $k_{d-w}$  depends on the different characteristics of the soil such as organic matter content (OMC), clay content and soil mineralogy etc. As an example,  $k_{d-w}$  of Pb positively correlates with the OMC, whereas for the Cd a great positive correlation was observed with the soil mineralogy. The  $k_{d-w}$  may vary site to site. Thus the effect of the  $k_{d-w}$  was also examined in the sensitivity analysis. The values chosen for the  $k_{d-w}$  are 1, 0.1, 10 times of the  $k_{d-w}$  of the study area. (Cd: 1.3E-02, 1.3E-03, 1.3E-01 and Pb: 1.4E-01, 1.4E-02, 1.4 m<sup>3</sup>/kg). The time taken for peak heavy metal concentration in the monitoring points was compared.

Table 3-1 Input parameters used for model simulation

Zone	Description	Symbol	Unit	Value	Reference
Aquifer	Porosity	$n_a$		0.4	Ohata et al., (2015)
	Hydraulic conductivity	$k_x, k_y$	m/s	1E-03	Ohata et al., (2015)
	Hydraulic gradient	$i$	-	0.06 (0.006, 0.12)*	Nagamori et al., (2014)
	Diffusion coefficient	$D_M$	m <sup>2</sup> /s	Cd: 6.0E-10 Pb: 7.9E-10	USEPA (199)
	Dispersivity	$\tau_x$	m	Cd: 10 Pb: 10	USEPA (199)
	Distribution coefficient	$k_{d-w}$	m <sup>3</sup> /kg	Cd:1.3E-02 Pb:1.4E-01	Paranavithana et al., (2013)
Waste unit	Initial concentration of heavy metal component	$C_{ws}$	mg/kg	Cd:3.63E-02 Pb:4.16E+00	Udayagee et al., (2017)
	Distribution coefficient	$k_{d-ws}$	m <sup>3</sup> /kg	Cd:1.3E-03 Pb:2.7E-03	Allison JD, And Allison TL, (2005).
PRB	Maximum adsorption capacity of heavy metal	$Q_m$	mg/kg	Cd:3.02E+03 Pb:9.94 E+02	Paranavithana et al., (2016)
	Langmuir isotherm constant	$b$	m <sup>3</sup> /mg	Cd:2.68E-04 Pb:4.54E-05	Paranavithana et al., (2016)
Meteorological parameters	Rainfall intensity	$q_r$	mm/yr	3.53 E+03	Udayagee et al., (2017)
	Permeation ratio	$R$	-	1	USEPA (199)

### 3.3 Results and Discussion

#### 3.3.1 Model Outputs of Sensitivity Analysis

Table 3.2 exemplifies the model outputs of sensitivity analysis. In both cases output values (peak time and concentration inside the PRB) were highly sensitive to the hydraulic gradient for both heavy metals. For example, the time for peak concentration was mainly controlled by  $i$ : the time taken to reach the maximum HM concentration at a particular point for  $i = 0.006$  become 4-6 times higher than that for  $i = 0.06$ . On the other hand, the effect of pollution load was significant only for the outputs from Case 2: the peak concentration for the low pollution load became ~20% of the peak concentration for the high pollution load.

Figure 3 shows the effect of distribution coefficient on the washing out of the heavy metals in the aquifer. The effect of  $k_{d-w}$  was significant for the heavy metal concentration and the rate of the washing out process. The peak heavy metal concentration was higher and the less time was taken to reach breakthrough with the decreasing of  $k_{d-w}$ . According to Alumaa et al., (2001) the soil rich with organic matter may have high  $k_{d-w}$  for Pb which encourage the slow releasing, whereas the soil rich with Ca may enhance the Cd immobilization (high  $k_{d-w}$ ) and slow washing out process.

As shown in Table 2, the washing out of contaminants (reduction in metal concentration) was much faster in Case 2 than Case 1 for both Cd and Pb. This attributes to the direct exposure of waste unit into the groundwater flow in Case 2. On the other hand, the washing out of heavy metals is controlled only by the rainfall precipitation in Case 1. These results reveal that a rapid and higher contamination in the surrounded aquifer is easily occurring for the waste dump site with a buried waste whereas in waste heaps prolong the washing



out process. Furthermore, the heavy metals trapped by the PRB in Case 2 were greater than those in Case 1 due to the higher concentrations of heavy metals in the inflow to PRB.

### **3.3.2 Evaluation of the Effectiveness of PRB**

The effectiveness of the virtual PRB was evaluated by considering the outflow HM concentrations. Fig. 3.2 illustrates temporal variations of the heavy metal concentrations at different points of the aquifer. In most cases, the PRB was able to well trap the heavy metals in the aquifer and reduced the peak concentration at the outflow from PRB. For both Cd and Pb, the heavy metal concentrations observed at the outflow from PRB were less than those of the effluent water quality standards in Sri Lanka which is <0.1 mg/L for Cd and Pb (CEA 2005).

### **3.3.3 Pollution Migration Process in the Aquifer**

Figure 3.3 shows an example of pollutant migration process in the aquifer. The simulation was carried out to observe the pollutant plume of Cd in the aquifer, with respect to the Case 2. As counter maps show there a rapid washing out process was observed in the upstream to the PRB and the pollutant plume reached to the PRB within six months. A drastic reduction of Cd concentration was observed in the outflow from the PRB due to the immobilization process at the PRB. However, even after 10 years, contaminants can be found in the aquifer which is 300 m away from the buried waste unit.

Table 3-2 Model outputs of sensitivity analysis

		Cd			Pb	
		<i>i</i>	Time (Year)	Concentration (mg/L)	Time (Year)	Concentration (mg/L)
High pollution load	Case 01	0.060	5.50	2.30E-03	41.7	2.44E-02
		0.120	3.70	2.18E-03	25.3	2.44E-02
		0.006	24.0	2.35E-03	148	2.17E-02
	Case 02	0.060	0.90	1.16E-02	6.70	1.40E-01
		0.120	0.50	1.22E-02	4.20	1.85E-01
		0.006	5.30	1.14E-02	39.7	1.40E-01
Low pollution load	Case 01	0.060	7.50	1.44E-03	78.2	1.67E-02
		0.120	4.60	1.30E-03	45.8	1.70E-02
		0.006	41.9	1.60E-03	N.B.*	N.B.*
	Case 02	0.060	2.80	2.54E-03	30.1	2.61E-02
		0.120	1.70	3.14E-03	17.8	4.12E-02
		0.006	17.7	2.44E-03	N.B.*	N.B.*

\*N.B.: No breakthrough.

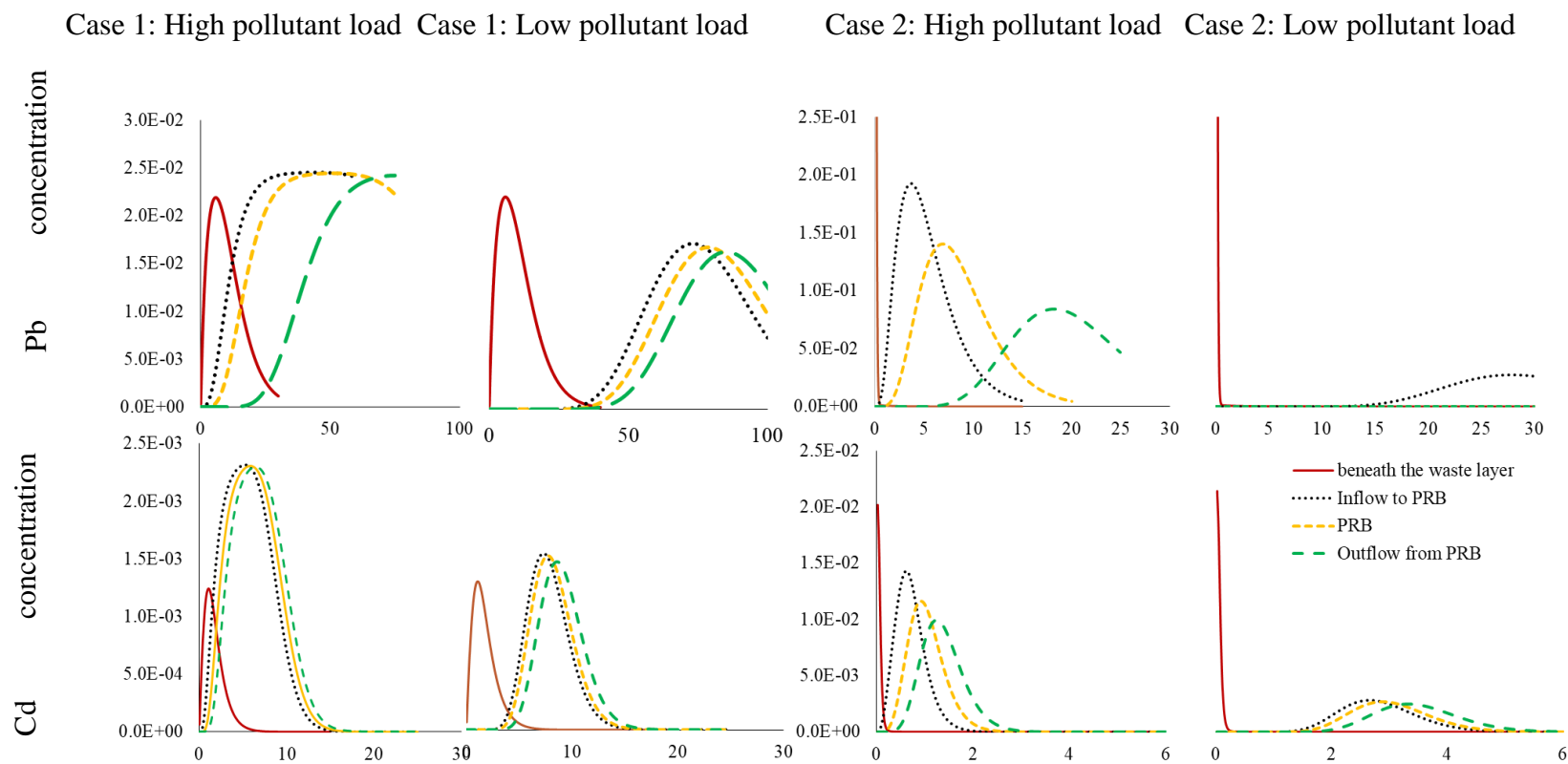


Figure 3-3 Temporal variation of the heavy metal concentration at the different locations of the aquifer for Cd and for Pb

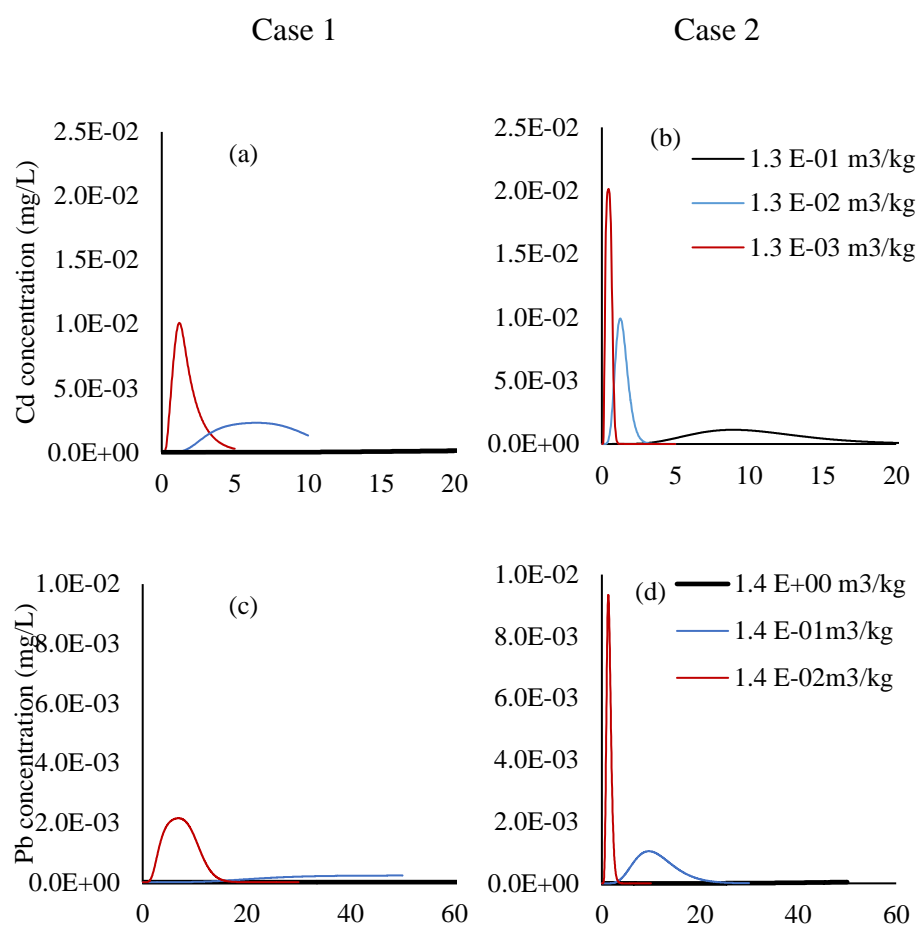


Figure 3-4 The model output of sensitivity analysis at different distribution coefficients Cd [(a), (b)] and for Pb [(c), (d)]

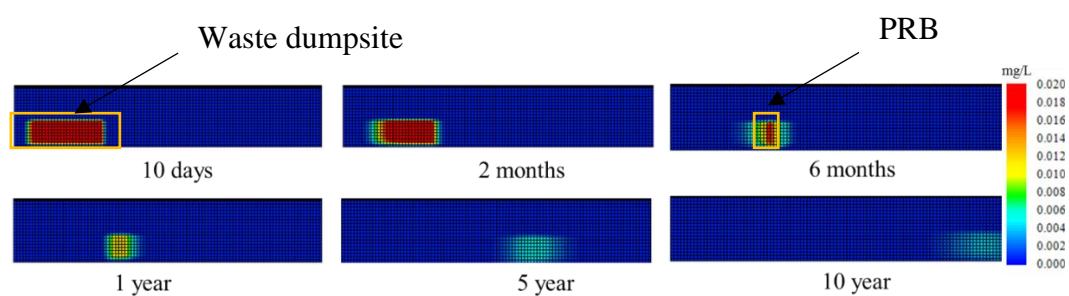


Figure 3-5 An example for pollution migration process in the aquifer

### 3.4 Conclusions

In this study, numerical simulations were used to understand the washing-out process of heavy metals from the pollutant source (waste unit). The effectiveness a virtual PRB consist with a selected material (soil 50% + Bichar 50%) was evaluated by comparing heavy metal concentration at upstream and downstream points to the PRB. The time period needed for the full washing-out was highly dependent on the range of hydraulic gradient, pollution load, distribution coefficient and the way of waste dumping. The PRB well trapped the targeted heavy metals and reduced the contamination level less than the effluent water quality standard. The reactivity and hydraulic conductivity of PRB materials should be well characterized prior to the actual field implementations.

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# **Chapter 04. EVALUATION OF APPLICABILITY OF FILLING MATERIALS IN PERMEABLE REACTIVE BARRIER (PRB) SYSTEM FOR GROUNDWATER REMEDIATION: BATCH STUDY**

## **Abstract**

The groundwater contamination is a serious issue observed at open solid waste dumpsites. Low cost, easily manageable treatment mechanisms are highly demanded to avoid and minimize the future risk of groundwater contamination. In this study, the applicability of locally available adsorbents was tested for their reactivity and hydraulic properties to use as the PRB filling materials at the contaminated groundwater bodies. The targeted contaminants were Cd and Pb which having high severity and vulnerability in groundwater pollution surrounded by open solid waste dumpsites. Mixtures of alluvial loamy soil, coconut shell biochar, and laterite clay brick in different proportions were tested as low-cost and locally-available PRB adsorbents. A series of Adsorption and desorption experiments were carried out to investigate the effects of initial concentration, pH, ionic strength, and multiple competitive trace elements on Cd and Pb adsorption onto the tested adsorbents. In addition, hydraulic conductivities ( $K_s$ ) of the tested adsorbents under different compaction levels were measured to examine a suitable packing condition for the PRB system. Results showed that the Langmuir model performed well for fitting Cd and Pb adsorption isotherms for the whole range of initial metal concentrations (<2000 mg/L) and maximum adsorption capacities for Pb became higher than those for Cd. All tested adsorbents showed low leaching of adsorbed metals with high hysteresis indices in desorption studies. In the multiple trace element solution, the existence of other metals had a significant effect on Cd adsorption but less on Pb adsorption. The inclusion of brick was



effective to improve the hydraulic property and measured  $K_s$  values for 75% brick materials gave results of  $>10^{-4}$  cm/s at high compaction levels ( $D_r = 90\%$  and  $100\%$ ). Three mixed materials can be strongly recommended as a low-cost PRB filling material to treat landfill leachate generated in Sri Lanka based on their reactivity and hydraulic properties.

#### **4.1 Introduction**

The ground-water supplies throughout the world are contaminated or threatened, in an accelerated way by wastewater plumes containing organic, inorganic contaminants, radionuclides and heavy metals (B.J. Alloway, 2013; Mulligan et al., 2001). The potential sources of groundwater contamination are improper management of chemical storages tanks, septic systems, uncontrolled hazardous wastes, chemicals and road salts, agrochemicals (Wong et al., 2002) atmospheric contaminants and open waste dumping etc (Chaney et al., 2004; Grimm et al., 2008; Sewwandi et al., 2014; Udayagee et al., 2017). Especially the heavy metals such as Pb, Cd, Cu, Zn are most common contaminants observed in the groundwater surrounded by open solid waste dumpsites, caused by industrial waste dumping (Sewwandi et al., 2013; Wijesekara et al., 2014). Effective remediation techniques are needed to reduce the risk of spreading the contaminated water plume throughout the aquifers and minimize the negative effects on the ecosystem.

Groundwater extraction and ex-situ treatment are used widely (Naftz and Davis, 1999) as a method of contaminated ground-water remediation and discharge of the treated water, commonly known as pump and treat. Ex-situ treatment methods are costly and often ineffective in meeting long-term protection standards (USEPA, 1999). Thus it is suggested the implementation of Permeable Reactive Barriers (PRB) as a new and potentially cost-effective technology for removal of contaminants from groundwater (Carey et al., 2002)

The concept has been developed to take advantage of natural groundwater gradient to flow contaminated water through the highly permeable reactive material, (Carey et al., 2002; Regmi, 2009) instead of pumping up the water as used in ex-situ treatment techniques (Naftz and Davis, 1999). As the groundwater flow passes through the PRB, the contaminant is immobilized or transformed to a non-toxic form due to variety of chemical reactions (sorption, degradation and precipitation) occurring in/on the reactive barrier materials (Di Natale et al., 2008; Obiri-Nyarko et al., 2015; Thiruvengkatachari et al., 2008). PRB technology for groundwater treatment has been studied widely (Zhou et al., 2014), approximately 624 of laboratory and field scale studies have been done between 1999-2009.

A thorough understanding of adsorptive capacities and permeability is needed prior to implementing a PRB, to ensure the efficient immobilization of contaminant and maintain the passive flowing (Carey et al., 2002; USEPA, 1999). Many reactive media combinations can be used in PRBs and numerous media and mixtures of media are being investigated for a variety of contaminants. Zero-valent iron (ZVI),  $\text{Fe}^0$ , has been used widely as a PRB material (Statham et al., 2015; Suzuki et al., 2012), and as reported in ITRC (2005), more than 60% of PRBs were made of ZVI by 2004. The greater reduction potential ( $-440 \text{ mV}$ ) and precipitation capacity augment the transfer of electrons to contaminants by activating various chemical reactions. In addition to ZVI, zeolite (Vignola et al., 2011), calcite (Turner et al., 2008), and  $\text{FeS}$ -coated sand (Han et al., 2011) have been used as PRB filling materials in various field scale and laboratory scale studies. Further several biomaterials have tested their reactive capacities to use as heavy metal adsorbents which are potential materials to be used as PRB filling materials. Coconut husk (Sewwandi et al., 2014), crab shells (Vijayaraghavan et al., 2011), forest biowaste (Kim et al., 2015) sawdust (Sewwandi et al., 2012), rice straw (Xu et al., 2017) are some of the examples of potential sorbets.

In addition to the reactivity, the hydraulic conductivity of PRB material under different compactions should be evaluated since it is a highly important factor which determines the performance of the PRB. The compacted reactive material in the barrier whose hydraulic conductivity is greater than that of the surrounding soils ensures that groundwater spontaneously flows through the barrier without any external energy input. Thus it is important to select granular formed reactive media or the media mixed with some granules, in order to achieve the targeted hydraulic conductivity.

In the current study, three materials and their mixtures with different proportions were tested for adsorptive, desorptive and hydraulic performances on Pb and Cd removal from contaminated groundwater. Two materials were selected based on a past research study (Paranavithana et al., 2016). Local soil and coconut shell biochar collected from Sri Lanka has a significant removal efficiency over solution phase Pb and Cd. Additionally, in this study, burnt laterite brick was tested for the PRB media, with the purpose of enhancing hydraulic performances of the barrier, which is abundantly found in Sri Lanka. Thus the objectives of this study were to 1. Investigate the adsorption and desorption behavior of the selected materials and mixtures 2. Evaluate the hydraulic performances of the selected materials and mixtures 3. evaluate the applicability of our tested materials to treat groundwater contaminated with landfill leachate.

## **4.2. Materials and Methods**

### **4.2.1 Materials used**

Table 01 exemplify the basic physical and chemical characteristics and fig. 4.1 shows the materials used in this study. Local soil and biochar were selected as PRB testing materials, by referring Paranavithana et al., (2016) They have found that both tested soils and biochar has a greater adsorption capacity on Pb and Cd in aqueous media.

A local soil (hereafter soil) from Bangadeniya, North Western Province, Sri Lanka, is a loamy alluvial soil and is categorized as an Entisol in the FAO classification system (Kang and Tripathi 2015; FitzPatrick 1980; Mapa et al. 2010;). The soil is a sandy clay loam soil which recognized as naturally acidic (Mapa et al. 2010). According to the Paranavithana et al. (2013) Bangadeniya soil is rich in micropores in the range from 0.5 to 50  $\mu\text{m}$ , which are effective for water retention. Further, the surface charge of the Bangadeniya soil was predominantly permanent and the soil has high CEC. The soil was expected to better adsorb heavy metals and was chosen as a testing material which is commonly available in Sri Lanka. The soil was prepared for the experiments by air drying, sieving with 2mm meshes and keeping their natural moisture contents by storing in sealed polyethylene bags.

Coconut shell biochar (hereafter biochar), is an inexpensive and amply available material in tropical countries including Sri Lanka (Babel and Kurniawan. 2004) was used as a testing material in this study. The biochar was crushed and fine granules were obtained by passing through a 75 $\mu\text{m}$  sieve, in order to facilitate better mixing with other tested materials. The coconut shell biochar is an alkaline material and consists of the greater surface area which is important to maximize the adsorption capacities. (Paranavithana et al., 2016). Further, the presence of predominant functional groups is a clue of better adsorption of the cations such as  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  and other cationic heavy metal forms (Liu and Zhang 2009).

Burnt laterite brick (hereafter brick) commonly available in Sri Lanka, was crushed, sieved and coarse granular particles ( $2.00 < D < 4.75 \text{ mm}$ ) were used as a testing material. Though the brick has been identified as a good heavy metal adsorbent at lower contaminant concentrations (Sadia et al 2014; Rabiaa et al., 2006) the main objective of using brick was to enhance the hydraulic performances of the barrier.

In this study, aforementioned three materials were mixed in different percentages and nine PRB testing materials were prepared to analyze their adsorption and hydraulic properties. The nine mixed PRB testing materials were Soil 100%, Biochar 100%, Brick 100%, Soil 50% + Biochar 50%, Soil 75% + Biochar 25%, Soil 25% + Biochar 75%, Soil 25% + Biochar 25% + Brick 50%, Soil 37.5% + Biochar 37.5% + Brick 25%, and Soil 12.5% + Biochar 12.5% + Brick 75%.



Figure 4-1 The tested materials

Table 4-1 Basic physical and chemical properties of tested materials

	Soil		Biochar		Brick	
Location	Bangadeniya,	Sri	Matale,	Sri	Kandy,	Sri
	Lanka		Lanka		Lanka	
Particle size (mm)	< 2.00		< 0.075		2.00 - 4.75	
Moisture content in air dry (%)	3.4		3.2		0.4	
pH	4.7		8.8		5.4	
EC ( $\mu\text{S}/\text{cm}$ )	59		139		47	
BET surface area ( $\text{m}^2/\text{g}$ )	28.5		212		14.4	
Specific gravity	2.66		1.51		2.77	
Loss on ignition (%)	12.3		60		0.9	

#### **4.2.2 Batch experiments for adsorption and desorption studies**

Test conditions for batch adsorption and desorption experiments are summarized in Table 2. Batch adsorption and desorption experiments were conducted by referring standard batch method recommended by the Organization of Economic Cooperation and Development (OECD 2000).

All the experiments were conducted with 1:10 solid: liquid ratio. HM solutions were prepared by using  $\text{PbCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$  salts (<99.5 %, Wako Pure Chemical Industries, Ltd., Japan). Clean 50 mL Violamo centrifuge tubes (AO1350002, Sigma-Aldrich, USA) were used to shake the testing materials and solutions. Samples were shaken in a reciprocating shaker for 24h at 100 rpm at 20°C temperature. After shaking, samples were centrifuged at 8000 g for 15 min and supernatants were filtered through a membrane filter (Millipore 0.23  $\mu\text{m}$ ). Then, the supernatants were diluted into predetermined dilution factors and measured contaminant concentrations by atomic adsorption spectrophotometry (AA 6200, Shimadzu, Japan). For every experiment triplicate samples were used.

#### **4.2.3 Effect of initial metal ion concentration on adsorption**

Batch adsorption experiments were carried out for nine test adsorbents at natural pH by changing initial metal ion concentrations for Cd and Pb from 100–2000 mg/L. The adsorption behavior of was studied, by fitting the data into isotherm models; Linear (Eq. 4.1), Freundlich (Eq. 4.2) and Langmuir (Eq. 4.3) models (Bulgariu and Bulgariu. 2012; Cheng et al.,2012). The contaminant removal efficiency was estimated by referring Eq. 4.4.

The Linear model is purely empirical and should be applied only to conditions under which the  $K_d$  was measured. This is advantageous over other models since it is a simple model

and it can be applied to complex matrices which would be difficult to obtain all the required mechanistic surface adsorption data. The Linear model is expressed as follows.

$$Q_e = K_d C_e \quad \text{Eq 4.1}$$

where  $Q_e$  = amount adsorbed per kg of adsorbent at equilibrium (mg/g),  $C_e$  = equilibrium aqueous metal ion concentration (mg/L) and  $K_d$  = distribution coefficient (L/g).

The Freundlich model is applied to non-ideal adsorption equilibrium on heterogeneous surfaces and also to multi-layer adsorption, suggesting that binding sites are not unique. The model has been developed based on following assumptions. 1) there is an infinite supply of unreacted adsorption sites, 2) stronger binding sites are occupied first and binding strength decreases with the increasing degree of site occupation 3) there is a logarithmic reduction of the affinity between solute and adsorbent during surface coverage. The Freundlich model is expressed as follows.

$$Q_e = K_f C_e^n \quad \text{Eq 4.2}$$

where  $K_f$  = Freundlich adsorption capacity (L/g) and  $n$  = adsorption intensity.

The Langmuir isotherm model is based on the following assumptions: 1) the adsorption sites are homogeneous, 2) the adsorption is limited to monolayer coverage, 3) all sites are energetically and sterically independent for the amount of adsorbed, and 4) the adsorptive forces are similar to the forces in the chemical interaction (Febrianto et al., 2008; Limousin et al., 2007]. The Langmuir equation is expressed as follows:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad \text{Eq 4.3}$$

where,  $b$  = Langmuir constant related to binding strength (L/mg), and  $Q_m$  = maximum adsorption capacity.

The removal efficiency was calculated following equation.

$$R = [(C_i - C_e)/C_i] \times 100 \quad \text{Eq 4.4}$$

where  $R$  = removal efficiency (%) and  $C_i$  = initial aqueous metal ion concentration (mg/L).

#### **4.2.4 Effect of initial pH and background ion concentration on adsorption**

Experiments were conducted to determine the effect of initial pH on the adsorption mechanism for nine tested materials. Adsorption experiments were performed using a Cd solution with the initial concentration of 300 mg/L and a Pb solution with the initial concentration of 350 mg/L in the pH range from 4 to 10 at three ionic strengths (0.1, 0.01, 0.005M). The pH values for metal ion solutions were adjusted by adding either 0.1 M sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl). The background ion concentration was changed by adding NaNO<sub>3</sub>.

#### **4.2.4. Desorption experiments**

Desorption experiments were conducted to study leaching of adsorbed metals from the tested materials. First, the batch adsorption process was facilitated by mixing 1g of testing adsorbent and 10 ml of heavy metal solution. The initial concentrations used were 300 and 350 mg/L for Cd and Pb respectively. Then, 24 h equilibrated samples were centrifuged, and 7 mL of supernatant was taken out from each 10 mL sample solution. The same time, the suspension was refilled with 7 ml of pure water, and samples were shaken for equilibration. Consecutive desorption procedure was repeated two more times to obtain a complete desorption isotherm with three desorption points. The experimental outputs were modeled with Freundlich isotherm equation to obtain hysteresis index. The desorption hysteresis index was estimated with respect to the difference between adsorption isotherm and a desorption isotherm (Ma et al., 1993). The hysteresis index, (%), was calculated as follows (Eq 4.5).



$$\omega = \left[ \left( \frac{n_a}{n_d} \right) - 1 \right] \times 100 \quad \text{Eq 4.5}$$

Where,  $n_a$  = adsorption intensity and  $n_d$  = desorption intensity calculated refereeing to Freundlich isotherm model.

#### **4.2.5 Effect of Competitive Ion on Adsorption**

Adsorption experiments were conducted to study the effect of competitive ions on adsorption onto testing adsorbents. A mixture of heavy metal solution ( $\text{PbCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{ZnCl}_2$ ) was prepared as the initial concentration of each heavy metal to be 300 mg/L. The adsorbents and metal solution were mixed with 1: 10 solid to liquid ratio and adsorption experiment proceeded at the same experimental condition. The adsorption efficiency was compared with the % removal ( $R$ ).

Table 4-2 Testing conditions for adsorption and desorption studies

	$C_i$ (mg/L)	pH	Background electrolyte
[Single trace element solution: Cd, Pb]			
1. Effect of initial metal concentration on adsorption	0, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1250, 1500, 1750, 2000 mg/L	Natural pH ~5	H <sub>2</sub> O
2. Effect of pH and background ion concentration on adsorption	300 mg/L for Cd and 350 mg/L for Pb	pH <sub>i</sub> = 4, 5, 6, 7, 8, 9, 10	0, 0.005, 0.01, 0.1M NaNO <sub>3</sub>
3. Desorption of adsorbed metals	300 mg/L for Cd and 350 mg/L for Pb	Natural pH ~5	H <sub>2</sub> O
[Multiple-trace element solution: Cd, Pb, Cu, Ni, Zn]			
4. Adsorption	300 mg/L for Cd, Pb, Cu, Zn, Ni	Natural pH ~5	H <sub>2</sub> O

#### 4.2.6 Compaction and hydraulic conductivity experiments

Hydraulic conductivity test was carried out for the tested materials with the different degree of compaction prepared by standard Proctor compaction (proctor A method, 1000 cm<sup>3</sup> volume core) or hand compaction (100 cm<sup>3</sup> volume core). Compaction tests were conducted with standard Proctor method to obtain compaction curve, giving maximum dry density according to JIS A 1210. For the hydraulic conductivity test, constant head method (Eq 4.6) was used for the samples having the hydraulic conductivity of 10<sup>-3</sup> to 10<sup>-5</sup> cm/s, while for the samples having the hydraulic conductivity of 10<sup>-5</sup> to 10<sup>-9</sup> cm/s, falling head method (4.7) was applied.

$$k_s = \frac{L}{h} \cdot \frac{Q}{A(t_2 - t_1)}$$

Where,  $K_s$  = Saturated hydraulic conductivity,  $L$  = length of the specimen,  $h$  = hydraulic head,  $A$  = cross-sectional area of the specimen,  $Q$  = quantity of water discharged  $t$  = time required to discharge  $Q$  amount of water.

$$k_s = 2.303 \frac{aL}{A(t_2 - t_1)} \log \frac{h_1}{h_2}$$

Where,  $a$  = cross-sectional area of the falling water head,  $h_1$  = initial height of the water head and  $h_2$  = final height of the water head.

### 4.3 Results and Discussion

#### 4.3.1. Effect of initial metal ion concentration on adsorption

The measured adsorption data for Cd and Pb were fitted to linear, Freundlich, and Langmuir isotherm models, Eqs (4.1, 4.2, 4.3) and Fig. 4.2 shows the measured and fitted Langmuir isotherm model. The fitted parameters for adsorption isotherm models and removal efficiencies are summarized in Table 4.3. The linear adsorption isotherm model

was fitted to measured adsorption from  $C_i < 400$  mg/L. The model was able to fit Pb adsorption for some of the tested combinations but not for Cd. (Table 4.3). The Freundlich adsorption isotherm model, performed well for fitting both Cd and Pb adsorption at low  $C_i$  conditions ( $< 400$  mg/L) (Table 4.3) by giving high regression coefficients, whereas at high initial concentrations the model was not fitted well with the measured data (Data not shown).

The Langmuir isotherm model was well fitted with the all measured for Cd and Pb for the whole range of  $C_i$  by giving high regression coefficients (Table 4.3 and Fig. 4.2). This indicates that the predominant homogeneous and monolayer adsorption mechanism of the adsorption of Cd and Pb onto the all the tested adsorbents. (Cheng et al., 2012). The  $Q_m$  values for Pb adsorption were ranged between 2.1–15.3 mg/g and higher than those for Cd adsorption (0.8–6.8 mg/g). For Cd adsorption, the  $Q_m$  value of biochar (6.8 mg/g) was lower than that of soil (2.9 mg/g) while the  $Q_m$  values of mixtures of soil and biochar ranged from 4.2 to 6.2 mg/g. For Pb adsorption, the  $Q_m$  values of soil and biochar were similar (15.1 and 15.3 mg/g), and the  $Q_m$  values of mixtures of soil and biochar became relatively constant, ranging from 12.6 to 13.7 mg/g. The  $Q_m$  values of brick-mixed materials decreased for Pb adsorption with increasing proportions of brick. On the other hand, for Cd adsorption, the  $Q_m$  values of brick-mixed samples became lower than non-brick-mixed ones but did not decrease with increasing proportion of brick.

Similar to previous studies of different adsorbents (Cheng et al., 2012; Paranavithana et al., 2016; Sewwandi et al., 2014), the removal efficiencies,  $R$  (%), for Pb adsorption became greater than those for Cd adsorption. In particular, the  $R$  values of tested adsorbents exceeded 90% excepting for brick 100% and a mixed brick sample with the high proportion of brick (Soil 25% + Biochar 12.5% + Brick 75%). This may govern by

the higher reactivity and low free energy in hydration of Pb which facilitate the fast adsorption process always (Park et al., 2016).

The mechanism of the adsorption was tried to understand by observing the pH changes before and after the adsorption process. The  $\Delta\text{pH}$  (= pH after adsorption – pH before adsorption) calculated at half saturation,  $0.5 Q_m$ , and full saturation of heavy metal adsorption,  $Q_m$ , are summarized in Table 4. 4. A different pattern of  $\Delta\text{pH}$  changes was observed for Pb and Cd adsorption onto the soil (Soil 100%). The pH values increased slightly at  $0.5 Q_m$  and did not change at  $Q_m$  after Cd adsorption, while the pH values decreased after Pb adsorption. For the biochar (Biochar 100%), the  $\Delta\text{pH}$  values always increased after the adsorption of both Cd and Pb. For the brick (Brick 100%), the  $\Delta\text{pH}$  values decreased at  $Q_m$  after the adsorption of Cd and Pb.

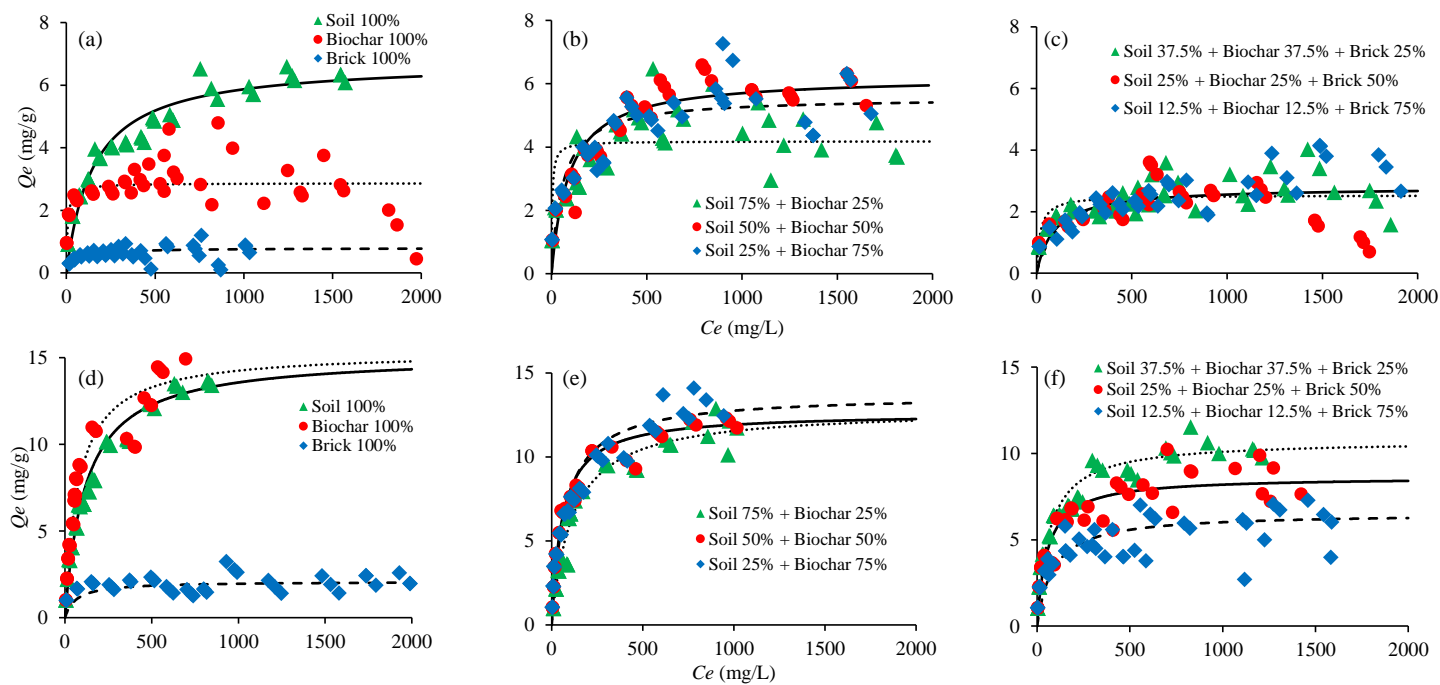


Figure 4-2 Measured adsorption isotherms (triplicate measurements) and fitted curves of Langmuir isotherm model for Cd [(a), (b), (c)] and Pb [(d), (e), (f)]

Table 4-3 Fitted parameters for adsorption and desorption isotherm models ( $K_d$ ,  $K_{fa}$ ,  $n_a$ ,  $K_{fd}$ ,  $n_d$ ,  $Q_m$ , and  $b$ ), removal efficiency ( $R$ ), and hysteresis index ( $\square$ ) for tested adsorbents. NA = Not adoptable.

	Linear ( $C_i$ < 400mg/L)		Freundlich ( $C_i$ < 400 mg/L)							Langmuir ( $0 \leq C_i \leq 2000$ mg/L)			$R$ (%)
	$K_d$ (L/g)	$r^2$	Adsorption			Desorption				$Q_m$ (mg/g)	$b$ (L/g)	$r^2$	
			$K_{fa}$ (L/g)	$n_a$	$r^2$	$K_{fd}$ (L/g)	$n_d$	$r^2$	$\omega$				
<b>[Cd]</b>													
Soil 100%	NA	NA	0.34	0.45	0.99	2.02	$4.2 \times 10^{-2}$	0.62	$9.7 \times 10^2$	6.8	0.006	0.98	91
Biochar 100%	NA	NA	0.93	0.22	0.92	2.36	$1.4 \times 10^{-2}$	0.99	$1.4 \times 10^3$	2.9	0.136	0.92	98
Brick 100%	NA	NA	0.12	0.33	0.92	1.59	$3.0 \times 10^{-2}$	0.99	$1.0 \times 10^3$	0.8	0.019	0.90	65
Soil 75%+Biochar 25%	NA	NA	0.81	0.25	0.94	2.02	$3.8 \times 10^{-2}$	0.96	$5.5 \times 10^2$	4.2	0.242	0.94	96
Soil 50%+Biochar 50%	NA	NA	0.70	0.29	0.86	1.98	$5.4 \times 10^{-2}$	0.93	$4.3 \times 10^2$	6.2	0.011	0.98	95
Soil 25%+Biochar 75%	NA	NA	0.81	0.28	0.97	2.03	$5.5 \times 10^{-2}$	0.98	$4.1 \times 10^2$	5.5	0.017	0.94	97
Soil 37.5%+Biochar 37.5%+Brick 25%	NA	NA	0.40	0.32	0.98	1.87	$3.3 \times 10^{-2}$	0.94	$8.7 \times 10^2$	2.5	0.053	0.85	72
Soil 25%+Biochar 25%+Brick 50%	NA	NA	0.60	0.19	0.97	1.80	$2.3 \times 10^{-2}$	0.91	$7.2 \times 10^2$	2.8	0.010	0.96	70
Soil 12.5%+Biochar 12.5%+Brick 75%	NA	NA	0.40	0.28	0.97	1.27	$3.9 \times 10^{-2}$	0.83	$6.2 \times 10^2$	2.9	0.080	0.89	68
<b>[Pb]</b>													
Soil 100%	0.11	0.80	0.31	0.70	0.97	3.36	$2.3 \times 10^{-2}$	0.71	$2.9 \times 10^3$	15.1	0.008	0.99	95
Biochar 100%	0.16	0.85	0.24	0.88	0.89	3.04	$3.9 \times 10^{-2}$	0.69	$2.1 \times 10^3$	15.3	0.012	0.96	95
Brick 100%	NA	NA	0.71	0.18	0.86	1.66	$4.2 \times 10^{-2}$	0.89	$3.2 \times 10^2$	2.1	0.015	0.88	92
Soil 75%+Biochar 25%	NA	NA	0.48	0.73	0.91	2.41	$6.2 \times 10^{-2}$	0.88	$1.1 \times 10^3$	13.7	0.013	0.98	96
Soil 50%+Biochar 50%	0.19	0.94	0.26	0.90	0.98	3.1	$4.1 \times 10^{-2}$	0.95	$2.1 \times 10^3$	12.6	0.017	0.99	96
Soil 25%+Biochar 75%	NA	NA	0.14	0.85	0.98	3.18	$2.4 \times 10^{-2}$	0.88	$3.4 \times 10^3$	12.8	0.008	0.98	90
Soil 37.5%+Biochar 37.5%+Brick 25%	NA	NA	0.36	0.72	0.96	3.08	$6.7 \times 10^{-2}$	0.63	$9.7 \times 10^2$	10.7	0.015	0.99	96
Soil 25%+Biochar 25%+Brick 50%	0.12	0.41	0.54	0.57	0.95	3.00	$4.1 \times 10^{-2}$	0.84	$1.2 \times 10^3$	8.6	0.018	0.96	96
Soil12.5%+Biochar12.5%+Brick75%	0.06	0.03	0.71	0.39	0.94	2.65	$4.3 \times 10^{-2}$	0.97	$8.0 \times 10^2$	6.5	0.011	0.94	96

Table 4-4 .  $\Delta$  pH values at 0.5  $Q_m$  and  $Q_m$  for Cd and Pb adsorption onto tested adsorbents

Adsorbent	pH <sub>i</sub>	Cd		Pb	
		$\Delta$ pH at 0.5 $Q_m$	$\Delta$ pH at $Q_m$	$\Delta$ pH at 0.5 $Q_m$	$\Delta$ pH at $Q_m$
Soil 100%	5.2	0.2	0.0	-0.5	-0.6
Biochar 100%	5.2	2.7	2.1	1.4	0.7
Brick 100%	4.9	0.3	-0.2	-0.4	-0.7
Soil 75% + Biochar 25%	5.3	1.7	1.3	0.2	-0.2
Soil 50% + Biochar 50%	5.2	1.8	1.4	0.3	0.2
Soil 25% + Biochar 75%	5.3	1.5	1.2	1.0	0.5
Soil 37.5% + Biochar 37.5% + Brick 25%	5.1	1.6	1.3	1.3	0.1
Soil 25% + Biochar 25% + Brick 50%	5.2	1.4	1.2	0.7	0.0
Soil 12.5% + Biochar 12.5% + Brick 75%	5.3	0.8	0.6	-0.3	-0.2



For Cd adsorption, the  $\Delta\text{pH}$  values of tested mixtures (Soil + Biochar, Soil + Biochar + Brick) were positive at both  $0.5 Q_m$  and  $Q_m$ . On the other hand, the  $\Delta\text{pH}$  values of tested mixtures after Pb adsorption were positive at both  $0.5 Q_m$  and  $Q_m$ , but became negative for samples with a high soil mixture (Soil 75% + Biochar 25%) and a high brick mixture (Soil 12.5% + Biochar 12.5% + Brick 75%). It is noted that the  $\Delta\text{pH}$  values at  $Q_m$  were always lower than those at  $0.5 Q_m$  for all tested adsorbents. This might be attributed to the deprotonation process after the continuous metal adsorption toward the saturation (maximum adsorption capacity), as reported in previous studies for coconut shell biochar, which is rich in basic functional groups (Paranavithana et al., 2016) and loamy soils rich in active hydroxyl groups (Costa et al., 2010).

#### **4.3.2 Effects of initial pH and background ion concentration on adsorption**

Figure 4.3 shows the removal efficiencies of Cd and Pb for tested adsorbents at different  $\text{pH}_i$  (4–10) and ionic strengths (0.001, 0.01, 0.1 M  $\text{NaNO}_3$ ). The  $\text{pH}_i$  of the solution has a great influence on the adsorption process because it alters the surface charge properties of

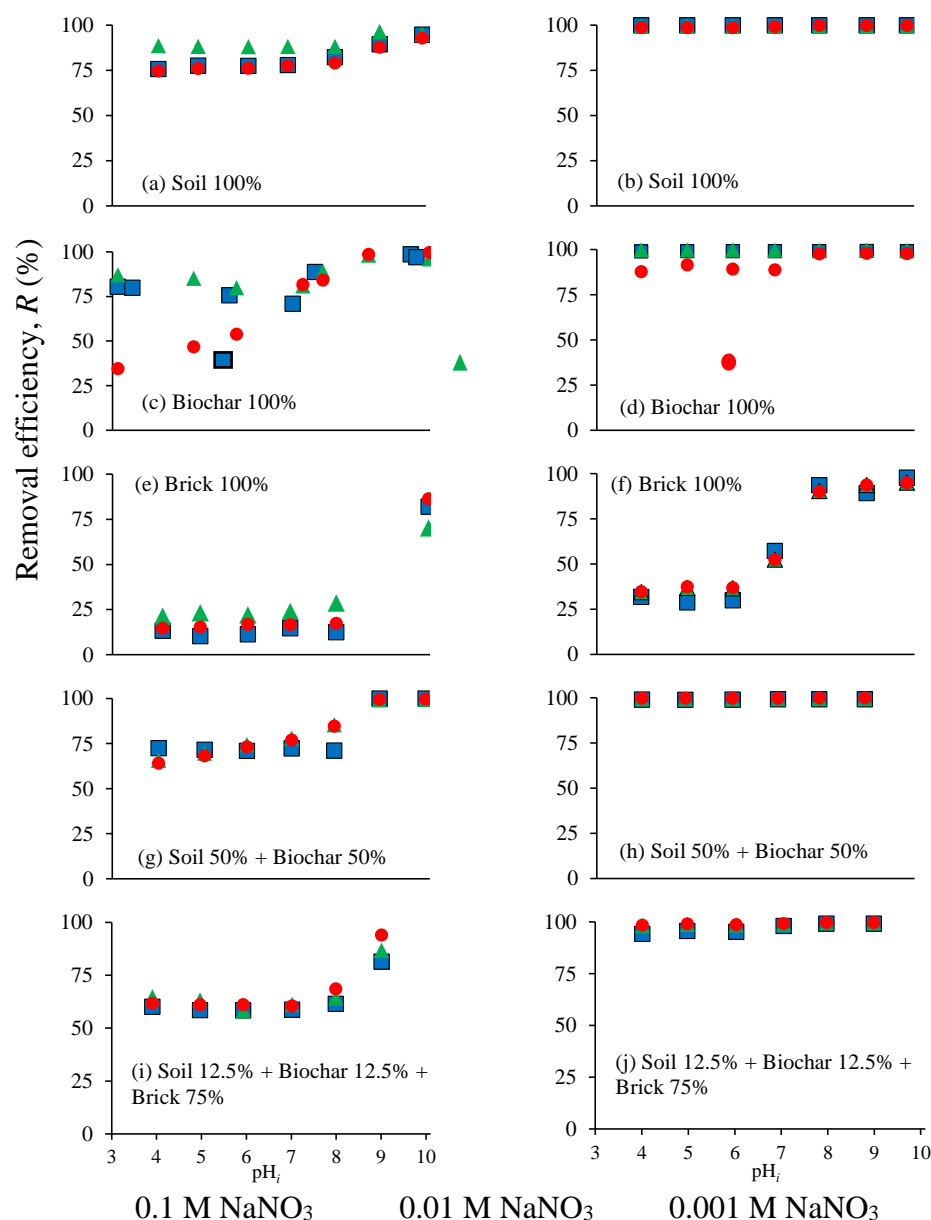


Figure 4-3 Removal efficiency,  $R$  (%), of Cd [(a), (c), (e), (g), (i)] and Pb [(b), (d), (f), (h), (j)] for tested adsorbents at different  $pH_i$  and ionic strengths

adsorbents and the degree of ionization (Park et al., 2016). Among tested soil, biochar, and brick, the removal efficiency of soil were relatively same at a whole range of  $pH_i$  and ionic strength (Fig. 4.3 a and 2b) while the brick showed a high  $pH$  dependence, i.e., the removal efficiency of brick varied from ~16 % at  $pH_i$  4–8 to ~80% at  $pH_i$  9 for Cd (Fig. 4.3 e and 4.3 f) and biochar showed a slight ionic strength dependency only for Cd adsorption (Fig. 4.3c).

The removal efficiency of Cd in tested mixtures, Soil 50% + Biochar 50% (Fig. 4.3 g) and Soil 12.5% + Biochar 12.5% + Brick 75% (Fig. 4.3 i), showed a slight dependency of  $pH_i$ . The removal efficiency increased in alkaline condition ( $pH > 9$ ). This is in accordance with the pH dependence brick. For Pb adsorption, on the other hand, the removal efficiency of tested mixtures (Figs. 4.3 h and 4.3 j) were independent of  $pH_i$  and became almost 100% in a whole range of  $pH_i$ . This indicates that even the brick 100% showed a  $pH_i$  dependency on Pb adsorption, the mixing of brick with soil and biochar could overcome the effect and give the high removal efficiencies. Compared to the effect of  $pH_i$  on the removal efficiency, the ion strength did not significantly affect the Cd and Pb removal. The removal efficiency of biochar for Cd adsorption was only affected by the differences in ionic strength, and low removal efficiency at  $pH_i$  4–6 were measured in the low ion strength condition (Fig. 4.3 c).

#### 4.3.3 Desorption experiments

The leaching behavior of the tested adsorbents was studied by carrying out the desorption experiments. The measured adsorption and desorption data (at low initial concentration) were modeled with Freundlich adsorption isotherm model [Eq (4.2)] to obtain parameters such as  $K_{fa}$ ,  $n_a$ ,  $K_{fd}$ , and  $n_d$ . For both adsorption and desorption isotherms, the model fitted with the measured data well, and the parameters are summarized in Table 4.3 together with the calculated values of the hysteresis index,  $\omega$  (%) [Eq. (5)]. Some examples for the fitted charts were shown in Fig. 4.4.

The desorption intensities,  $n_d$ , for all tested adsorbents (including three mixed materials), were two orders of magnitude lower than the adsorption intensities,  $n_a$ , resulted in high hysteresis for both Cd and Pb. This resulted in greater hysteresis index for both Pb and Cd and strongly suggests that the tested mixtures (soil, biochar, and brick) possess high

retention capacities and low leaching of adsorbed heavy metals, i.e., immobilization of adsorbed heavy metals. Especially, the  $\omega$  values for Pb exceeded  $8.0 \times 10^2$  for both mixtures of soil + biochar, and soil + biochar + brick. Similar results were observed by Hamidpour et al. (2010) for the adsorption of Pb onto zeolite and bentonite with 3500 and 1025, respectively. In the same study, the  $\omega = 173$  for Cd desorption from zeolite, and compare to this, our tested adsorbents showed a strong irreversibility for the bound metals, especially for Cd.

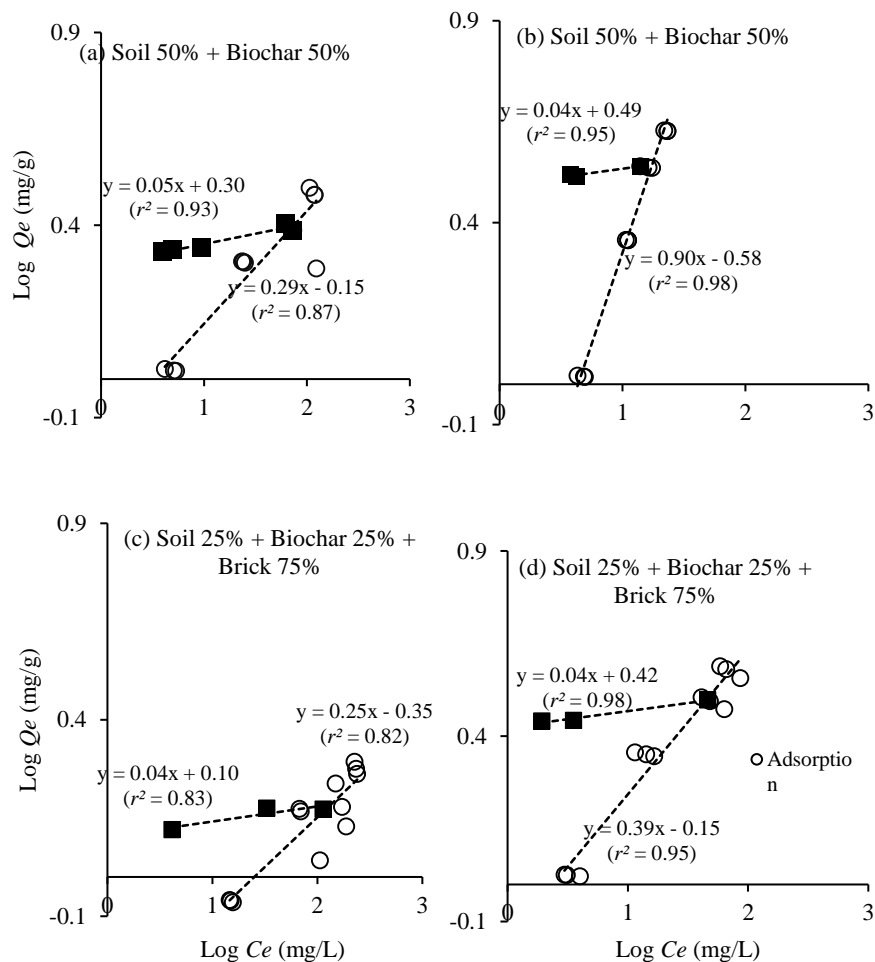


Figure 4-4 Adsorption and desorption isotherms fitted with Freundlich model for Cd [(a), (c)] and Pb [(b), (d)]. Fitted equations and  $r^2$  values are also given.

#### 4.3.4 Effect of competitive ions on adsorption

Figure 4.5 exemplifies the effect of competitive heavy metal ions (Cu, Zn, Ni) on Cd and Pb adsorption onto three tested adsorbents for mixtures of soil, biochar, and brick.

Observed sequences of adsorption for all tested adsorbents are given in Table 4.5. The existence of other heavy metals had a significant effect of adsorption of the targeted heavy metals (Cd and Pb in this study) in the multiple-trace metal solution, especially, the removal efficiency for Cd in the multiple-trace element solution became 1/3 of those in the single trace metal solution. Even though the Pb showed a greater selectivity among other metals for all the tested adsorbents (except Biochar 100%), the removal efficiency for Pb in the multiple- trace element solution (~60%) became lesser than those in a single trace metal element solution (~95). In general, a higher selectivity for Pb than Cu is observed for biochar and biochar-rich tested adsorbents. On the other hand, the Ni removal efficiency was increased with the increasing proportions of brick. Characteristics of heavy metals such as hydrated radius, atomic weight, hydrolysis constant, and Misono softness affect the metal adsorption and the resultant adsorption affinity of metals for adsorption sites (Park et al., 2016). In our tested adsorbents, the smaller hydrated radius is for  $\text{Pb}^{2+}$  (4.01Å) compared to other metals ( $\text{Zn}^{2+}$ : 4.30Å;  $\text{Cd}^{2+}$ : 4.26Å) and the greater affinity of Pb to most functional groups (carboxylic and phenolic groups present in biochar) might facilitate Pb adsorption onto tested adsorbents including biochar (Park et al., 2016).

There are several studies which report the reduction of removal capacities of the targeted heavy metals in the multiple-trace element solution, due to the competition with other heavy metals (Petrella et al., 2018; Srivastava et al., 2005). For example, Park et al. (2016) observed a drastic reduction of Cd adsorption onto sesame straw biochar in the multiple-trace element solution compared to that of the single trace element solution. Petrella et al. (2018) also reported the same scenario: Pb and Cd adsorption onto biosorbents derived from olive oil milling waste was reduced in the multiple-trace element solution than at the single trace element solution. The maximum adsorption capacities of both Pb and Cd were

reduced from 22.4 and 10.5 mg/g) to 10.51 and 5.11 mg/g when in a multiple-trace metal solution.

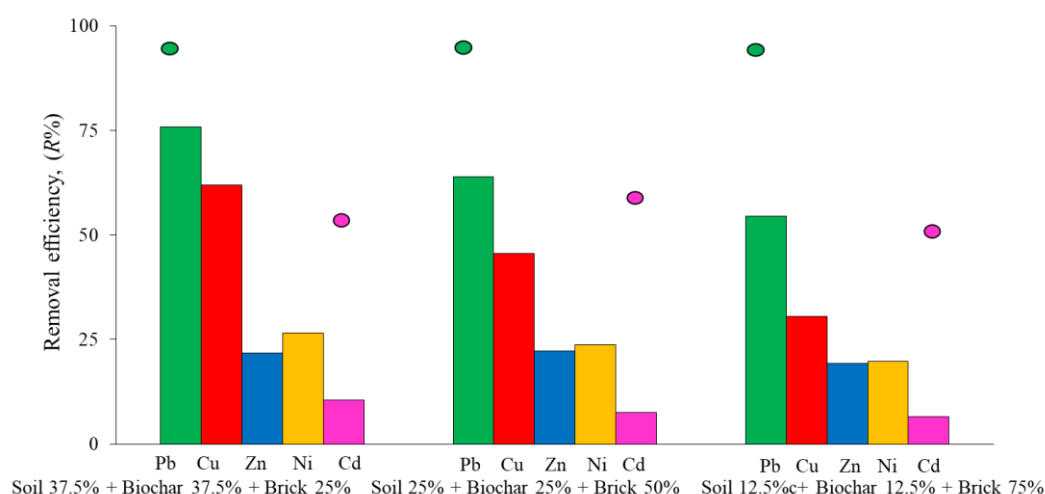


Figure 4-5 Measured removal efficiencies, R (%), from multiple-trace element solution tests. The R values from single trace heavy metal solution tests for Cd and Pb are also plotted.

Table 4-5 . Sequence of multiple-trace heavy metal adsorptions. Previously reported results are also given.

Adsorbent	Sequence of adsorption	References
Soil 100%	Pb > Cu > Zn > Ni > Cd	In this study
Biochar 100%	Cu > Pb > Zn > Ni > Cd	In this study
Brick 100%	Pb > Ni > Zn > Cu > Cd	In this study
Soil 75%+Biochar 25%	Pb > Cu > Zn > Ni > Cd	In this study
Soil 50%+Biochar 50%	Pb > Cu > Zn > Ni > Cd	In this study
Soil 25%+Biochar 75%	Pb > Cu > Zn > Ni > Cd	In this study
Soil 37.5%+Biochar 37.5%+Brick 25%	Pb > Ni > Zn > Cu > Cd	In this study
Soil 25%+Biochar 25%+Brick 50%	Pb > Ni > Zn > Cu > Cd	In this study
Soil 12.5%+Biochar 12.5%+Brick 75%	Pb > Ni > Zn > Cu > Cd	In this study
Sesame straw biochar	Pb > Cu > Cr > Zn > Cd	(Park et al., 2016)
Biosorbent from olive oil milling	Pb > Cd > Ni	(Petrella et al., 2018)
Montmorillonite	Pb > Cu > Ni = Zn = Cd	(Gu et al., 2010)

#### 4.3.5 Compaction and hydraulic conductivity experiments

The hydraulic conductivity of the packed PRB materials is one of the main selection criteria for the designing of better PRB which results in a minimal effect on groundwater flow, even though the PRB construction is likely to affect the background conditions of aquifers. The possible field problems can be overcome by increasing the hydraulic conductivity of filling materials in the PRB system (rather than the surrounding area) to allow groundwater to flow through the barrier using properly packed conditions (i.e., the degree of compaction of PRB materials).

Table 4.6 exemplify the results of compaction tests,  $\rho_{dmax}$  and  $w_{opt}$ , and measured hydraulic conductivities,  $K_s$ , at different compaction levels. In general,  $K_s$  values measured for all tested samples decreased with increasing degree of compaction ( $D_r$ ). Besides, with an increase in the mixed proportion of brick, the  $K_s$  increased. Especially, the  $K_s$  values for Soil 12.5% + Biochar 12.5% + Brick 75% exceeded  $10^{-4}$  cm/s even at higher compaction levels ( $D_r = 90\%$  and  $100\%$ ) compared to non-brick mixtures. The suitable degree of compaction and expected  $K_s$  for PRB will vary depending on the hydraulic properties of the surrounding conditions of ground and geological deposits.

However, typical  $K_s$  values range from  $10^{-3}$  to  $10^{-4}$  cm/s for loam soil and from  $10^{-4}$  to  $10^{-5}$  cm/s for silty loam soil (Kawamoto et al., 2006; Parrish, 1988). Compared to those values, the  $K_s$  values for tested materials with brick exceeded at  $D_r = 70\%$  and  $80\%$  or reached the Table 4.6 results of compaction tests,  $\rho_{dmax}$  and  $w_{opt}$ , and measured hydraulic conductivities,  $K_s$ , at different compaction levels

Table 4-6 Maximum dry density ( $\rho_{dmax}$ ), optimum moisture content ( $w_{opt}$ ), and saturated hydraulic conductivity ( $K_s$  in cm/s) at different compaction levels.

Material	$\rho_{dmax}$ (g/cm <sup>3</sup> )	$w_{opt}$ (%)	$K_s$ (cm/s)			
			Degree of compaction, $D_r$ (%)			
			70	80	90	100
Soil 100%	1.82	14.1	$1.7 \times 10^{-3}$	$1.4 \times 10^{-4}$	$3.8 \times 10^{-5}$	$2.0 \times 10^{-5}$
Brick 100%	1.18	15.1	$2.9 \times 10^{-2}$	$7.8 \times 10^{-3}$	$1.1 \times 10^{-4}$	$9.9 \times 10^{-5}$
Soil 75% + Biochar 25%	1.34	24.4	$1.1 \times 10^{-3}$	$1.1 \times 10^{-4}$	$2.6 \times 10^{-5}$	$1.3 \times 10^{-5}$
Soil 50% + Biochar 50%	1.12	34.8	$3.5 \times 10^{-4}$	$6.5 \times 10^{-5}$	$5.1 \times 10^{-5}$	$2.0 \times 10^{-5}$
Soil 25% + Biochar 75%	0.91	36.8	$3.7 \times 10^{-5}$	$1.6 \times 10^{-5}$	$1.1 \times 10^{-5}$	$9.1 \times 10^{-6}$
Soil 37.5% + Biochar 37.5% + Brick 25%	1.26	4.4	$3.9 \times 10^{-4}$	$1.5 \times 10^{-4}$	$2.5 \times 10^{-5}$	$2.5 \times 10^{-5}$
Soil 25% + Biochar 25% + Brick 50%	1.32	27.0	$2.0 \times 10^{-3}$	$7.0 \times 10^{-4}$	$2.1 \times 10^{-5}$	$2.5 \times 10^{-5}$
Soil 12.5% + Biochar 12.5% + Brick 75%	1.30	9.4	$2.6 \times 10^{-3}$	$2.0 \times 10^{-3}$	$1.5 \times 10^{-4}$	$1.0 \times 10^{-4}$



same order of magnitude at  $D_r = 90\%$  and  $100\%$ , indicating that our tested brick-mixed materials are suitable to ensure the water permeability through the PRB barrier.

#### **4.3.6 Applicability of tested adsorbents as filling materials to PRB system**

Reactivity and hydraulic conductivity are some of the key parameters that determine the robustness of the PRB filling materials, which have been examined in this study. Based on the results, the compatibility of tested materials to use as PRB filling materials to treat contaminated groundwater at open solid waste landfill sites is considered. As reported in previous studies (El-Gohary and Kamel, 2016; Naveen et al., 2017; Robinson, 2017; Sewwandi et al., 2013; Wijesekara et al., 2014), the Cd and Pb concentrations in landfill leachate observed  $< \sim 5$  mg/L, which can be achieved, R (removal efficiency)  $\sim 65\%$  by brick or brick-containing materials and  $\sim 90\%$  by other tested adsorbents in Cd removal, whereas  $\sim 90\%$  of Pb removal by all the tested adsorbents. The tested adsorbents (other than Cd adsorption onto brick) showed independent behaviors in Pb and Cd adsorption at different pH (4–10), which is an important characteristic to treat landfill leachate. Further, the adsorption of the tested materials (other than Cd adsorption onto biochar) was independent of the ionic strength (0.001–0.1M NaNO<sub>3</sub>) of the background solution. The three mixed adsorbents were strongly independent of the pH and ionic strength and showed higher removal efficiencies throughout the tested ranges. The pH and ionic strength of landfill leachates vary widely; depending on the phase of the degradation process, type of dumped waste, the degree of waste compaction, and interaction with the surrounding environment (Udayagee et al., 2017). Thus, the materials we tested can be strongly recommended for use as PRB filling materials in this scenario.

In the multi element solutions, Pb showed the greatest selectivity with a high removal efficiency ( $\sim 60\%$ ) among other tested heavy metals, which is a predominant and highly

toxic heavy metal present in the landfill leachate. Further, the removal efficiencies resulted in a satisfactory level for other competitive trace elements: Cu (~50%), Ni (~30%), and Zn (~25%).

The PRB filling materials should have very low desorption since the PRBs are continuously exposed to groundwater flow, and have a higher probability of detaching the bound heavy metals. The strength of metal binding onto the adsorbent and irreversibility of adsorption are strongly determined by the degree of desorption. The tested adsorbents showed very low desorption levels for the tested heavy metals by the resulting high hysteresis index. Especially, very low Cd leaching from our tested adsorbents was observed compared to zeolite, which is a commonly used PRB material. The study of metal desorption at different pH values is recommended with the compliment use of the tested adsorbents as PRB materials to treat landfill leachate since the pH of landfill leachates varies greatly.

The brick-mixed materials are recommended as PRB filling materials in consideration of their hydraulic conductivity at different packing density. Further, the three mixed materials do not corrode, and less clogging is expected during the treatment process; the soil and biochar may enhance the long-term reactivity while granular brick maintains the hydraulic conductivity. Thus, the mixture of these three materials ensures the targeted hydraulic conductivity ( $>10^{-4}$  cm/s) and enhances the longevity and sustainability, and reduces the cost of management, which are the key requirements of landfill leachate treatments in developing countries.

#### **4.4 Conclusions**

A series of adsorption, desorption and hydraulic conductivity tests were conducted to evaluate the reactivity and hydraulic properties of nine mixtures of locally available low

cost materials, to evaluate the applicability to use as PRB materials to treat groundwater contaminated with landfill leachate. The targeted heavy metals were Cd and Pb which is commonly available in landfill leachate and all the tested adsorbents (Soil, Biochar, Brick and their mixtures) were collected from Sri Lanka. The measured data from isotherm experiments fit the Langmuir isotherm model well, and the resulting  $Q_m$  values for Pb adsorption were higher than those for Cd. The Cd and Pb adsorption onto three mixed adsorbents were independent of pH and ionic strength, and the higher removal efficiencies (Cd: ~75% and Pb: ~95%) were observed throughout the tested pH range. In the multiple trace element solution, the removal efficiencies of targeted heavy (Cd and Pb) metals were reduced drastically but showed greater selectivity for Pb among the other heavy metals (Cu, Zn, Ni). All the tested adsorbents showed high retention capacities and low leaching of adsorbed heavy metals, resulting in higher hysteresis indices. Increased proportions of brick increased the hydraulic conductivity ( $>10^{-4}$  cm/s) at high compaction ( $D_r = \sim 90\%$ ) levels and were able to achieve the targeted field  $K_s$ . The tested adsorbents (three mixed materials) are strongly recommended as PRB filling materials to treat groundwater contaminated with landfill leachate based on their reactivity and hydraulic properties. Further studies (such as continuous flow-based studies) are essential to evaluate the long-term behavior of reactivity and hydraulic conductivity of our tested adsorbents for use as a robust PRB filling material.

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## **Chapter 05. EVALUATION OF APPLICABILITY OF FILLING MATERIALS IN PERMEABLE REACTIVE BARRIER (PRB) SYSTEM FOR GROUNDWATER REMEDIATION: A COLUMN STUDY**

### **Abstract**

Permeable reactive barriers systems are one of the effective and low-cost treatment technique in contaminated groundwater treatment. The low cost and locally available reactive materials (soil, Biochar, and brick) were collected from Sri Lanka and their long-term performance was evaluated using a column study in the treatment of Cd-contaminated water. The materials were air dried, sieved and mixed into a pre-desired ratio and packed into the column uniformly to achieve 80% of the degree of compaction. The Cd removal efficiency was evaluated at two initial concentration as 30 and 300 ppm. The effluent was collected and the breakthrough curves were obtained for both Cd and Br<sup>-</sup>. The removal efficiency with  $C_0 = 30$  ppm reached almost 100% throughout the tested duration, while the removal efficiency with  $C_0 = 300$  ppm reached 90% at the beginning and gradually reduced with the time. The hydraulic conductivity ( $K_s$ ) of tested materials were obtained at different EC to observe the hydraulic properties of the tested materials. Results showed that a linear correlation between  $K_s$  and EC.

### **5.1 Introduction**

Pollution of water resources is a major problem as it changes the quality of water. Water is polluted either intentionally or unintentionally by improper management of industrial waste, agricultural operations, shipping in the water bodies and open dumping of municipal waste dumping etc. The ground-water sources throughout the world are contaminated or threatened, in an increasing trend by wastewater plumes containing

organic, inorganic contaminants, radionuclides and heavy metals (Mulligan et al., 2001). The presence of toxic heavy metals in groundwater brings significant changes in properties of water and create the negative impact on environmental quality. Hence the removal of heavy metal from contaminated groundwater bodies has become a major challenge in environmental engineering. One of the promising technologies of treating contaminated groundwater is the pump and treat method. But this requires special technical knowledge and high cost in implementation and management. The Permeable Reactive Barriers (PRB) is a new and potentially cost-effective technology for removal of contaminants from groundwater in-situ (Carey et al., 2002). The main advantage of the PRB is the passive nature of contaminant removal.

A robust PRBs are consist with the materials of good reactivity and appropriate hydraulic properties. The efficiency of PRBs may reduce in the long term application since the changes in reactivity and hydraulic conductivity. Thus column based studies are highly important to study the adsorption mechanisms, reactions during the adsorption process and have more realistic data in long-term performances. Thus the objective of this study was to evaluate the long-term behavior of a selected mixture of adsorbent to use as PRB filling materials to treat Cd contaminated groundwater.

## **5.2 Materials and methods**

### **5.2.1 Selection of PRB materials and column preparation**

The tested materials were selected based on previous studies (Paranavithana et al. 2016, Udayagee et al., unpublished). In their studies the tested materials have been identified as effective PRB materials based on the reactivity and hydraulic properties, to treat contaminated water with Cd and Pb. All the tested materials were collected from Sri Lanka as low-cost adsorbents. A local, loamy alluvial soil (hereafter soil) was collected from

Bangageniya area, which is categorized as Entisol. The soil is a naturally acidic soil, according to the Paranawithana et al., (2013) Bangadeniya soil is rich in micropores in the range from 0.5 to 50  $\mu\text{m}$ , which are effective for water retention. Further, the surface The tested materials were selected based on previous studies (Paranavithana et al. 2016, Udayagee et al., unpublished). In their studies the tested materials have been identified as effective PRB materials based on the reactivity and hydraulic properties, to treat contaminated water with Cd and Pb. All the tested materials were collected from Sri Lanka as low-cost adsorbents. A local, loamy alluvial soil (hereafter soil) was collected from Bangageniya area, which is categorized as Entisol. The soil is a naturally acidic soil, according to the Paranawithana et al., (2013) Bangadeniya soil is rich in micropores in the range from 0.5 to 50  $\mu\text{m}$ , which are effective for water retention. Further, the surface charge of the Bangadeniya soil was predominantly permanent and the soil has high CEC. The soil well adsorbed the Cd in the aqueous media by giving  $Q_m$  as 7 mg/g (Udayagee et al., unpublished). The soil was air dried, sieved through 2mm meshes and kept under natural moisture contents by storing in sealed polyethylene bags.

Coconut shell biochar (hereafter biochar) is a commonly available material in Sri Lanka was used as a testing material. The coconut shell biochar has been identified as an alkaline material, consistent with a greater surface area and predominant functional groups which is important to maximize the adsorption capacities (Paranavithana et al., 2016). According to Udayagee et al., unpublished, the  $Q_m$  for Cd adsorption was 3 mg/g in aqueous media.

Laterite brick (hereafter brick) was used with the objective of increasing hydraulic conductivity of the PRB. Udayagee et al., unpublished, was observed that the increasing proportions of brick (in the mixtures of soil, biochar, and brick) increased the hydraulic conductivity at high packing densities ( $D_r = 80\%$ ) and was able to maintain the hydraulic conductivity to compatible with field requirements. The brick was collected from Kandy,

Sri Lanka was crushed, sieved and coarse granular particles ( $2.00 < D < 4.75$  mm) were used as a testing material.

The mixing proportions of these three materials were decided based on the Udayagee et al., unpublished. In this study the material mixing proportion was set to be soil 12.5%: biochar 12.5%: brick 75% based on the metal adsorption capacities, independence of the heavy metal adsorbent at different environmental conditions such as pH and ionic strength, metal immobilization (desorption), and hydraulic properties. Table 5.1 exemplify some basic physical and chemical properties of used materials and their mixtures (Udayagee et al., unpublished).

Table 5-1 The basic physical and chemical properties of used materials and their mixtures

	Soil	Biochar	Brick	Soil 12.5%: Biochar 12.5%: Brick 75%
Location	Bangadeniya, Sri Lanka	Matale, Lanka	Sri Kandy, Lanka	Sri
Particle size (mm)	< 2.00	< 0.075	2.00 - 4.75	
$W_{ad}$ (%)	3.4	3.2	0.4	
pH	4.7	8.8	5.4	
EC ( $\mu\text{S}/\text{cm}$ )	59	139	47	
BET surface area ( $\text{m}^2/\text{g}$ )	28.5	212	14.4	
Specific gravity	2.66	1.51	2.77	
Loss on ignition (%)	12.3	60	0.9	
$Q_m$ (mg/g) – Cd	6.8	2.9	0.8	2.9
$K_s$ at $D_r = 80\%$	$1.4 \times 10^{-4}$	NM	$7.8 \times 10^{-3}$	$2.0 \times 10^{-3}$

### 5.2.2. The effect of EC on hydraulic conductivity of the column filled materials

The hydraulic conductivity ( $K_s$ , cm/s) of tested material was observed at different ionic strengths. The saturated hydraulic conductivity of the tested materials were measured at  $D_r$  (%) = 80% with different EC (0.1, 0.25, 0.5, 1 mS/ cm) solutions prepared with  $\text{CaCl}_2$ . For  $K_s$  measurements, constant head method was used for the samples packed with hand compaction into  $100 \text{ cm}^3$  volume cores.

### 5.2.3 Column experiment

The initial moisture content of mixed materials was adjusted to  $w_i = 5\%$ , by adding water and the properly mixed filling materials were carefully filled into the column to achieve  $1.04 \text{ g/cm}^3$  of packing density, ( $D_r = 80\%$ ). Stainless steel filters (pore size 1 mm) were placed top and bottom of the column to avoid the washing out of packing media and the column was saturated gradually, by providing a small water head. The artificial contaminated water was prepared by dissolving  $\text{CdCl}_2$  and  $\text{NaBr}$  ( $<99.5\%$ , Wako Pure Chemical Industries, Ltd., Japan) with distilled water. Two column experiments were carried out to evaluate the Cd removal efficiency at different initial Cd concentrations (30 and 300 mg/L) while  $\text{Br}^-$  concentration was kept as 80 mg/L.

The experiments were conducted to flow water up to 30 total pore volumes (PV) through the column. First, the background solution (artificial rainwater) was flowed until 5 PVs and then shifted to Cd solution until it reaches 25 PVs. Then the column was washed again with the background solution by flowing water up to total PV reaches 30. The pH, EC, Cd and  $\text{Br}^-$  concentrations of effluent water were measured periodically and the hydraulic conductivity of effluent flow was monitored simultaneously throughout the experimental sessions. The output data will be analyzed with HYDRUS 1D software to determine the reactivity and solute transfer mechanisms inside the column.

The Cd removal efficiency,  $R\%$  in the column was calculated using Eq. 01

$$R\% = \left[ \frac{\text{Cumulative amount of Cd inflow (g)} - \text{Cumulative amount of Cd outflow (g)}}{\text{Cumulative amount of Cd inflow (g)}} \right] \times 100\%$$

A schematic diagram of the column experimental setup is shown in Fig. 5.1 and the basic information of column is exemplified in Table 5.2.

Table 5-2 Basic information of the column

Parameter	Value
Height of the column (cm)	30
Cross sectional area of the column (cm <sup>2</sup> )	19.6
$\rho_d$ (g/cm <sup>3</sup> )	1.04
Total porosity or 1 PV (cm <sup>3</sup> )	351.5
Dr (%); [= packed dry density/ $\rho_{dmax}$ x 100 (%)]	80
Hydraulic gradient	0.33
Inlet concentrations: Cd (mg/L)	300, 30
Inlet concentration: Br (mg/L)	80

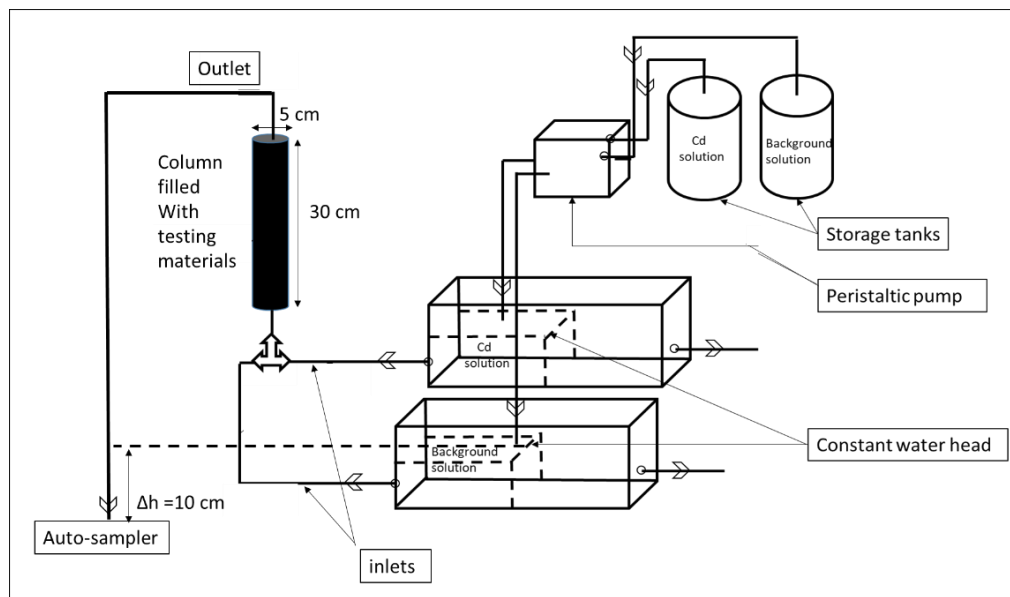


Figure 5-1 Schematic diagram of the apparatus used in the column experiment

## 5.3 Results and discussions

### 5.3.1 The effect of EC on $K_s$

Figure 5.2 shows measured saturated hydraulic conductivities of our tested materials at different EC. The average  $K_s$  observed at corresponding EC of two column experiments also were illustrated in the same fig. The saturated  $K_s$  of the tested materials increased linearly, with increasing EC of the solute. The corresponding  $K_s$  values observed in the



column experiments also well captured the fitted curve. Lower  $K_s$  values for lower EC conditions would be caused by the existence of Smectite clay in our used alluvial soil.

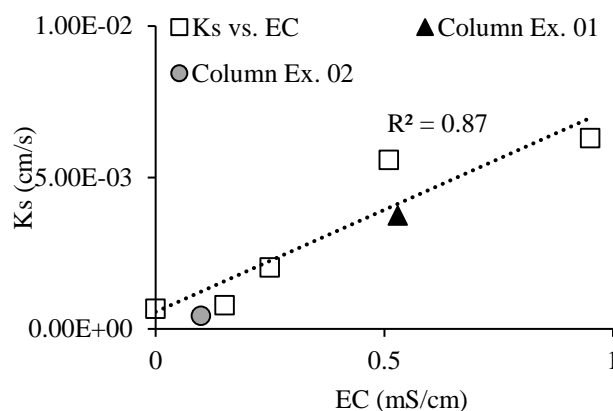


Figure 5-2 The effect of EC on saturated  $K_s$  of the tested material. The monitored  $K_s$  of column experiments were also plotted.

### 5.3.2 Breakthrough curves

The breakthrough curves were developed for both Cd and Br<sup>-</sup> measured in the effluent collected from both column experiments. Fig. 5.3 shows the Changes in the Cd and Br<sup>-</sup> concentration with the PV. In column Ex. 01, ( $C_i$  of Cd = 300 ppm) an efficient Cd removal ~90% up to 2 PV was observed at the beginning. Then the Cd concentration in effluent water increased with a decreasing rate. There was no breakthrough observed in the Cd concentration in the column Ex. 02 ( $C_i$  of Cd = 30 ppm). However, the ~100% removal of the Cd was observed throughout the tested duration. The Cd removal efficiencies observed at different PVs in both experiments were exemplified in Table 5.2. Br<sup>-</sup> behaved differently inside the column and no adsorption was observed. This reveals the different adsorption behavior of Cd<sup>2+</sup> (cation) and Br<sup>-</sup> (anion) onto the tested adsorbents. Further studies and numerical analysis are required to fully understand these mechanisms.

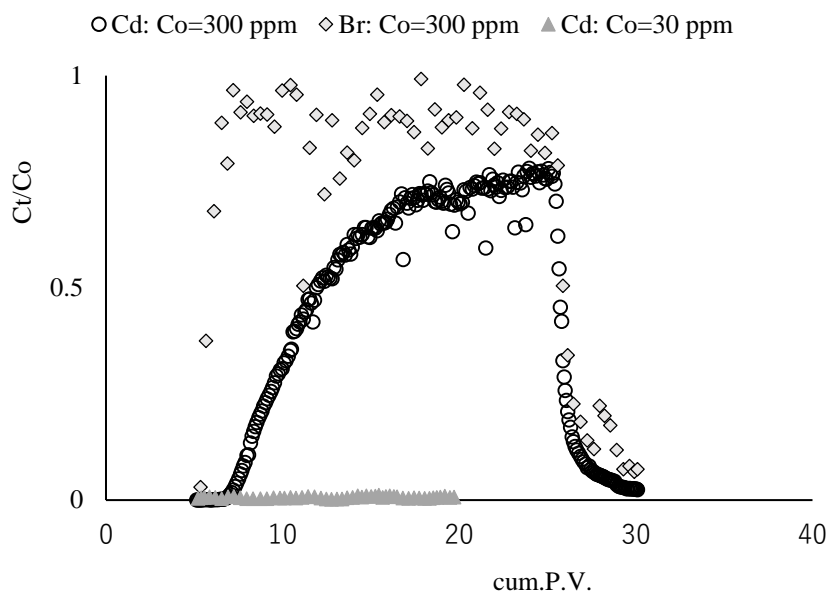


Figure 5-3 The breakthrough curves for Cd and Br; [ $C_t/C_o$  = (ion concentration at time t) / (ion concentration of inlet solution)]

Table 5-3 The Removal efficiencies (R%) of Cd in column experiments

	R% of the Cd solution		
	0-5 PVs	0-10 PVs	0-20 PVs
$C_o$ of Cd = 30 ppm	99.6	99.5	99.5
$C_o$ of Cd = 300 ppm	85.3	69.1	56.2

## 5.4 Conclusions

This study was conducted to evaluate the long-term reactivity and hydraulic performances of a selected adsorbent to use as a PRB filling materials. The effectiveness of the filling materials was tested at two initial Cd concentrations (30 and 300 ppm). The removal efficiency observed in column ex. 01, ( $C_i$  = 300 ppm) reached 90% at the beginning and gradually reduced with the time while in column ex. 02, ( $C_i$  = 30 ppm) the R%, reached almost 100% throughout the tested duration.

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## **Chapter 06. SUMMARY, CONCLUSIONS AND PERSPECTIVES**

### **6.1 Temporal variations in perched water and groundwater qualities at an open solid waste dumpsite in Sri Lanka**

An abundant solid waste dumpsite was monitored for 2 years, evaluate the water quality fluctuations in leachate and groundwater at the study area. The dumpsite has two sections namely Old section and New section based on the age of the usage. The old section has been used for 7 (2003-2010) years of dumping and the new section was used only for 6 months (2011) of dumping. Pollutant parameters such as BOD, COD, TOC, Major cations/anions, and heavy metals and some onsite parameters such as pH, EC, water temperature were measured periodically with respect to the standard procedures. The results shows that the groundwater samples from both Old and New sections had lesser contamination levels than the perched water. This seems to be the presence of the two independent water bodies in the dumpsite as the local perched water aquifers and groundwater aquifers in both Old and New sections. The BOD, COD, TN, TP of the perched water at New sections of the dumpsite was fluctuated at high concentrations. Even though TN at Old section was lower than the New section, always exceeded the WHO drinking water quality standards. EC of the perched water at new section showed high values; it is higher than 10 times that of perched water at old section and groundwater at both sections. This reveals the presence of high ionic concentration at the perched water at New section and reduction of inorganic ions in leachate with the age of the dumping. Heavy metals such as Pb, Cd, Cu, Zn, Cr etc. was observed both in perched water and groundwater and a less fluctuation was observed throughout the monitoring session. The leachate pollution index (LPI) was used to analyze the risk of environmental pollution and its temporal fluctuation. This index quantify the severity of contamination with respect to

organic contaminants, inorganic contaminants and heavy metals by its three sub-indices. The  $LPI_{in}$ ,  $LPI_{or}$  and  $LPI_{overall}$  calculated for perched water at new section was 3 - 4 times higher than perched water and groundwater at old section. Weather data such as rainfall, were collected from a nearby rain gauge station. There is a slight negative correlation was observed between rainfall and perched water quality. Finally, it can be concluded as the age of the dumpsite is a major factor that governs the landfill leachate quality.

## **6.2 Simulation of two-dimensional heavy metal transport in an aquifer at solid waste dumpsite: estimating the effectiveness of a permeable reactive barrier on heavy metal pollution control**

In this case study, Geo-Environmental Risk Assessment System (GERAS), a two-dimensional groundwater model has been used to simulate the heavy metal transport in an aquifer at solid waste dumpsite and to estimate the effectiveness of PRB on trap heavy metals. In the simulation, the targeted heavy metals were set to be Pb and Cd based on the results of research part 1. Two scenarios were examined: 1. An open dumping of waste (pollutant source) located above the aquifer (direct intrusion of rainfall through waste layer) and 2. A buried dumped waste inside the aquifer (no intrusion of rainfall). The effectiveness a virtual PRB consist with a selected material (soil 50% + Biochar 50%) was evaluated by comparing heavy metal concentration at upstream and downstream points to the PRB by changing the hydraulic gradient, initial pollution load and heavy metal distribution coefficients in the aquifer. The numerical simulations well captured the wash-out process of heavy metals from the pollutant source and the time period needed to have of full wash-out was highly dependent on the hydraulic gradient, pollution load, distribution coefficient and the way of waste dumping (case 1/ case2). Though the virtual PRB trapped the target metals and the downstream heavy metal concentrations were reduced less than the effluent water quality standards, the reactivity and hydraulic

conductivity of PRB materials should be well characterized prior to the actual field implementations.

### **6.3 Evaluation of applicability of filling materials in Permeable Reactive Barrier (PRB) system for groundwater remediation**

In this section of the research, aimed to identify appropriate permeable reactive barrier (PRB) filling materials to treat groundwater contaminated with heavy metals, in of solid waste landfills in Sri Lanka. The potential contaminants were selected as Cd and Pb based on the past studies on leachate quality analysis. Mixtures of alluvial loamy soil, coconut shell biochar, and laterite clay brick mixed in different proportions were tested as low-cost and locally-available materials. The effectiveness of PRB materials was evaluated by conducting adsorption, desorption, compaction and hydraulic conductivity testes. In the adsorption experiments, the effects of initial concentration, pH, ionic strength, and multiple competitive trace elements on Cd and Pb adsorption onto the tested adsorbents were studied. Results showed that the Langmuir model performed well for fitting Cd and Pb adsorption isotherms and maximum adsorption capacities for Pb became higher than those for Cd. All tested adsorbents showed low leaching of adsorbed metals (Cd and Pb) by resulting high hysteresis indices in desorption studies. Further, the three mixed materials resulted in a low dependency of pH and ionic strength in the adsorption of both metals. In the multiple trace element solution, the existence of other metals had a significant effect on Cd adsorption but less on Pb adsorption. .The hydraulic conductivities (Ks) of the tested adsorbents under different compaction levels were measured to examine a suitable packing condition for the PRB system. The inclusion of brick was effective to improve the hydraulic property and measured Ks values for 75% brick materials gave results of  $>10^{-4}$  cm/s at high compaction levels ( $D_r = 90\%$  and  $100\%$ ). The tested adsorbents (three mixed materials) are strongly recommended as PRB filling materials to

treat groundwater contaminated with landfill leachate based on their reactivity and hydraulic properties.

#### **6.4 Evaluation of applicability of low cost adsorbents as permeable reactive barrier (PRB) filling materials: a column study**

This study was conducted to evaluate the long-term reactivity and hydraulic performances of a selected adsorbent to use as a PRB filling materials. The low cost and locally available reactive materials (soil, Biochar, and brick) were collected from Sri Lanka and air dried, sieved into predetermined particle sizes. The column filled materials (Soil 12.5% + Biochar 12.5% + Brick 75%) were selected based on the research part 3. The three mixed material was packed into the column uniformly to achieve 80% of the degree of compaction, gradually saturated, and the Cd removal efficiency was tested at two initial Cd concentrations (30 and 300 ppm), at the same time Br<sup>-</sup> was flowed together with Cd as a non-reactive contaminant. The experiments were conducted to flow water up to 30 total pore volumes (PV) through the column. First, the background solution (artificial rainwater) was flowed until 5 PVs and then shifted to Cd solution until it reaches 25 PVs. Then the column was washed again with the background solution by flowing water up to total PV reaches 30. The pH, EC, Cd, and Br<sup>-</sup> concentrations of effluent water were measured periodically and the hydraulic conductivity of effluent flow was monitored simultaneously. The removal efficiency (R%) was highly depended on the initial Cd concentration; at  $C_0 = 300$  ppm the R% reached 90% at the beginning and gradually reduced with the time while in at  $C_0 = 30$  ppm the R%, reached almost 100% throughout the tested duration. Cd and Br<sup>-</sup> behaved differently; no adsorption of Br<sup>-</sup> was observed onto the PRB filling materials. The hydraulic conductivity (Ks) of tested materials were obtained at different EC to observe the hydraulic properties of the tested materials. Results

showed that a linear correlation between  $K_s$  and EC. The hydraulic conductivity of the filling material was drastically reduced at low EC.

## **6.5 Conclusions and Perspectives**

This study was mainly focusing on the development of site-specific permeable reactive barrier (PRB) systems to treat contaminated groundwater at the solid waste dumpsites in Sri Lanka. First, a case study was done at a Sri Lankan open solid waste dumpsite, to identify the current possible contaminants, the factors affecting leachate quality, and their temporal variation as the primary information for the PRB design. Several hazardous materials were observed in the leachate at the study area, including heavy metals such as Pb and Cd. Further, a slightly negative relationship was found between leachate quality and rainfall. The contamination level greatly reduced with the waste aging.

With the accordance of these pieces of information, a numerical simulation was performed to predict the future risk and evaluate the effectiveness of a virtual PRB set in a conceptual contaminated aquifer. Model well captured the pollutant transport process in the aquifer. The time taken to washing-out of contaminants was greatly depended on the initial contaminant concentration, hydraulic gradient, distribution coefficient of the heavy metal in the aquifer, and the way of waste dumping (direct dumping/buried waste dumping). The virtual PRB which is a mixture of alluvial soil and coconut shell biochar, well trapped the contaminants. It was noted that the washing-out process and PRB performances greatly depended on the site characteristics and management practices at the dumpsite.

Since the virtual PRB used in numerical simulation did not fully cover the geophysical and geochemical characterization of the reactive media, a series of laboratory experiments were conducted to evaluate their reactivity and hydraulic performances. Same materials (alluvial soil and coconut shell biochar) were used for the analysis, additionally, crushed



laterite brick granules were mixed with the reactive materials to make their hydraulic conductivities suitable for a permeable barrier system. The reactivity of the selected materials and their different mixtures were estimated at different initial pH, ionic strength, at the presence of different competitive heavy metals since a great variability of leachate quality has been observed during the case study. Among tested, Soil 12.5% + Biochar 12.5% + Brick 75% mixture was identified as the best suitable mixture, based on their independence in metal adsorption, low desorption, and the hydraulic performances. Then these materials were tested for their long-term performances by conducting series of a column experiment. The metal removal efficiency greatly depended on the initial contaminant concentration, whereas the hydraulic conductivity greatly depended on the EC of the flowing solution. An excellent removal efficiency of Cd was noted (~100%), at low initial concentrations, which represents the actual field contaminant concentrations.

In future perspectives of this study, the actual field performances of the tested PRB materials should be evaluated in a pilot field scale study, before the move into the large-scale field applications. Based on the laboratory findings, such as maximum metal binding capacities, suitable packing densities, and the field information, actual PRB design can be performed as shown in the fig. 6.1. Further, the field monitoring should be conducted frequently, to ensure the performances of the PRB.

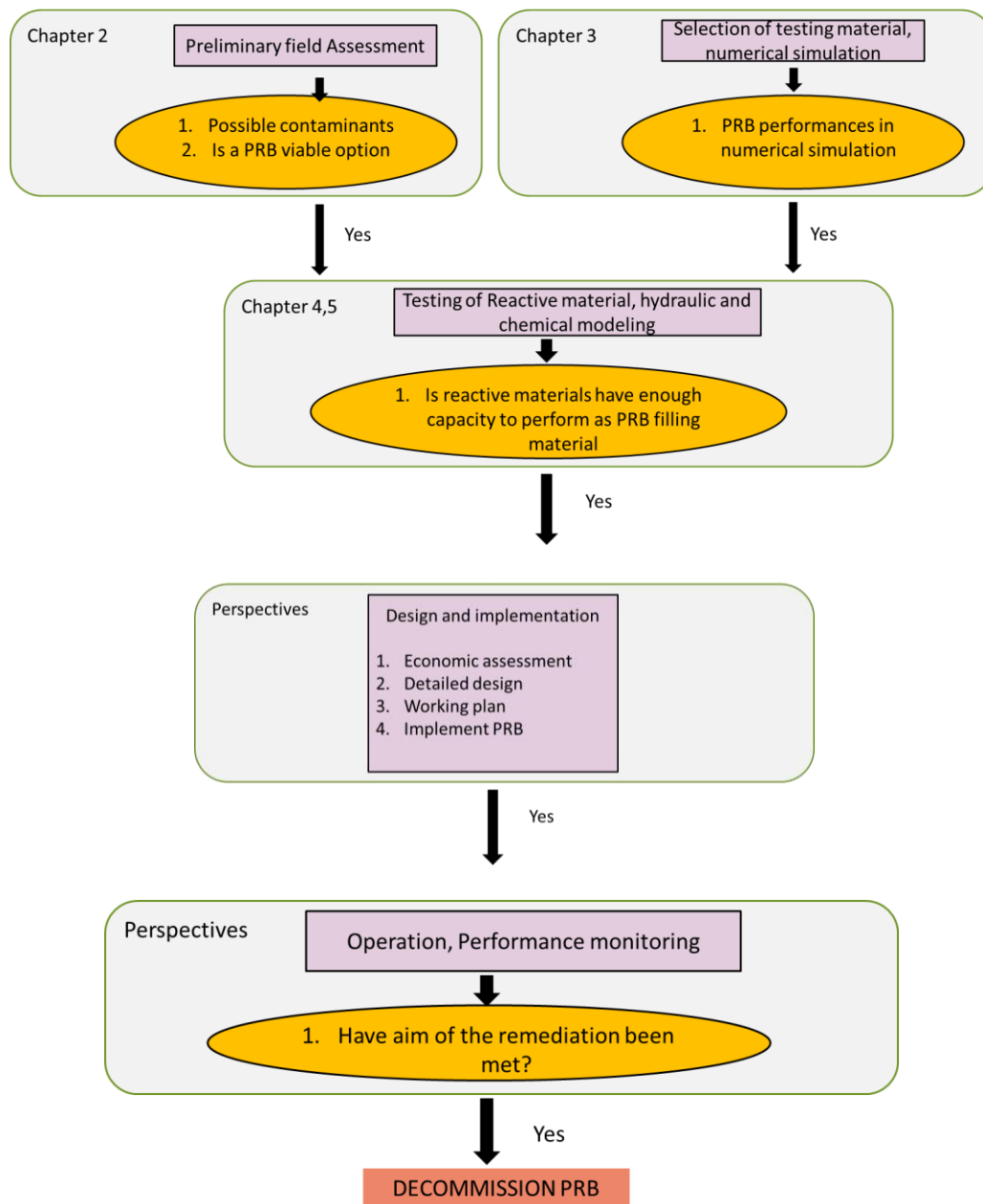


Table 6-1 Overall procedure for the assessment of permeable reactive barriers

## LIST OF PUBLICATIONS

### Journal publications

1. **Udayagee Kumarasinghe**, Ken Kawamoto, T. Saito, T., Sakamoto Y., and Mowjood, M.I.M. Evaluation of applicability of filling materials in Permeable Reactive Barrier (PRB) system to remediate groundwater contaminated with Cd and Pb at open solid waste dump sites. (Accepted on 17<sup>th</sup> August 2018, Journal of Processes Safety and Environmental Protection)
2. **Udayagee Kumarasinghe**, Inoue Y., Saito T., Nagamori M., Mowjood M.I.M., Kawamoto K. (2017). Temporal variations in perched water and groundwater qualities at an open solid waste dumpsite in Sri Lanka .int. j. geomate., 13:1-8.
3. **Udayagee Kumarasinghe**, Sakamoto Y., Saito T., Nagamori M., Kalpage C.S., Herath G.B. Mowjood M.I.M., Kawamoto K. (2017). Simulation of two-dimensional heavy metal transport in an aquifer at solid waste dumpsite: estimating the effectiveness of a permeable reactive barrier on heavy metal pollution control. (Accepted on 4<sup>th</sup> June 2018).

### Reports:

1. JST-JICA SATREPS project: Water Quality Monitoring at Udapalatha Open Solid Waste Dumpsite in 2013 & 2014.

### Peer reviewed conference papers

1. Saito R., **Udayagee Kumarasinghe**, Paranavithana G.N., Saito T., Kawamoto K. (2017). Development of permeable reactive barrier system utilizing locally available geo- and bio-waste. International conference on Advances in Civil and Environmental Engineering Practices for Sustainable Development Faculty of Engineering, University of Ruhuna, Galle, Sri Lanka 16<sup>th</sup> March 2017

2. **Udayagee Kumarasinghe**, Inoue Y., Saito T., Nagamori M., Mowjood M.I.M., Kawamoto K. (2016). Identification of temporal variability of contamination in perched water and groundwater at an open dumpsite in Sri Lanka, using Leachate Pollution Index (LPI). International conference on Advances in Civil and Environmental Engineering Practices for Sustainable Development Faculty of Engineering, University of Ruhuna, Galle, Sri Lanka 3<sup>rd</sup> March 2016
3. **Udayagee Kumarasinghe**, Saito T., Nagamori M., Mowjood M.I.M., Kawamoto K. (2016). Review on Variations in water quality for perched water inside waste and groundwater close by open dumpsites. 22<sup>nd</sup> symposium on Soil and Groundwater Contamination and Remediation. Kyoto University, Kyoto, Japan, 23-24<sup>th</sup> May 2016.

### **Conference abstracts**

1. **Udayagee Kumarasinghe**, Fernando W.A.P., Priyankara N., Pinnawala M., Iijima S., Kawamoto K. (2016). Evaluation of public and local authority awareness on solid waste management at Hambantota Municipal Council. 4<sup>th</sup> International conference on Sri Lanka- Japan collaborative research, University of Peradeniya. Sri Lanka. 19-21 August, 2016.
2. **Udayagee Kumarasinghe**, Inoue Y., Saito T., Nagamori M., Sakamoto Y., Mowjood M.I.M., Kawamoto K. (2016) Temporal variability of contamination in perched water and groundwater at an open dumpsite in Sri Lanka, using Leachate Pollution Index (LPI). Japan Geoscience union meeting, Makuhari Messe, Japan. 22<sup>nd</sup> -26<sup>th</sup> May 2016.
3. **Udayagee kumarasinghe**, Kawamoto K., Saito T., Sakamoto Y., Mowjood M.I.M. Evaluation of applicability of low cost adsorbents as permeable reactive barrier (PRB) filling materials: A column study. (Accepted on 3<sup>rd</sup> June 2018).