CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

With the increasing demand for water and competition for water between domestic, industrial and agricultural sectors, the quality problem becomes the limiting factor in the development of water resources. To meet the increasing demand for quality water, besides surface run-off, groundwater could be and has been utilised as a potential source of water supply. Groundwater can be contaminated through surface water due to human activities on its exploitation (Azuhan Muhammad, 1998). The sorption mechanisms of various contaminants such as heavy metals are controlled by physico-chemical and biological processes (Hoehn and von Gunten,1985). To evaluate the applicability of laboratory results, field measurements are essential for the natural groundwater system (Erdal et al, 1984 ; Jackson et al., 1980).

4.2 Heavy metals and their concentrations

Since the sites under study are agricultural and small scale industrial areas and can even be considered as having both activities, elements such as calcium (Ca), cadmium (Cd) and lead (Pb) are expected. These are attributed to the use of agrochemicals, pesticides and fertilizers (Chen et al., 1997; Ghestem and Besmond, 1998). Heavy metals like nickel (Ni), copper (Cu), zinc (Zn) and ferum (Fe) are also expected from the contents of the interstitial water since there are industrial activities that are involved with iron and steel e.g. grill making etc (Perin et al., 1997; Teixeira et al, 1997). If Fe is present, it is also advisable to check for the presence of Mn, since the two elements are readily adsorbed to one another (Pyeong et al., 1997, Perin et al., 1997). The heavy metals studied [extracted from the interstitial water derived from the soil secured by rig drilling] include Ca, Cd, Zn, Pb, Ni, Fe, Mn and Cu. Tables 4.1 to 4.5 list the heavy metal concentrations (in mg/l) at various depth intervals for the five sites studied. The results given are averages of three replicates.

Table 4.1 Heavy metal concentrations (mg/l) from Site 1 (near Port Klang)

Heavy Metal	Depth (m)			
	(0 - 10)	(10 - 20)	(20 - 30)	(30 - 40)
Ca	22.12	57.84	43.46	24.5
Pb	0.74	0.72	0.41	0.92
Ni	0.03	0.01	0.104	0.00
Fe	0.12	0.51	10.84	0.29
Mn	0.01	6.38	5.76	6.19
Cu	0.01	0.20	0.02	0.01
Cd	0.26	1.55	0.29	0.62
Zn	0.07	115.93	0.66	0.59

Table 4.2 Heavy metal concentrations (mg/l) from Site 2 (near Tol Shahpadu)

Heavy Metal	Depth (m)			
	(0 - 10)	(10 - 20)	(20 - 30)	(30 - 40)
Ca	21.88	8.96	15.1	-
Pb	0.26	0.24	0.08	-
Ni	0.01	0.05	0.10	-
Fe	0.22	0.12	0.1	-
Mn	0.01	0.14	0.2	-
Cu	0.01	0.05	0.01	-
Cd	0.18	0.17	0.19	-
Zn	0.51	1.59	4.45	-

Table 4.3 Heavy metal concentrations (mg/l) from Site 3 (Sg. Lang)

Heavy Metal	Depth (m)			
	(0 - 10)	(10 - 20)	(20 - 30)	(30 - 40)
Ca	19.36	12.21	17.99	10.51
Pb	0.29	0.20	0.74	0.70
Ni	0.01	0.01	0.01	0.01
Fe	0.28	0.15	0.76	0.83
Mn	0.01	0.01	0.01	0.01
Cu	0.01	0.01	0.01	0.01
Cd	0.03	0.10	0.08	0.02
Zn	0.01	0.01	0.08	0.01

Table 4.4 Heavy metal concentrations (mg/l) from Site 4 (landfill)

Heavy Metal	Depth (m)			
	(0 - 10)	(10 - 20)	(20 - 30)	(30 - 40)
Ca	56.70	34.78	35.96	14.02
Pb	0.51	0.01	0.62	0.82
Ni	0.05	0.05	0.01	0.01
Fe	5.96	9.96	0.25	0.38
Mn	0.27	0.01	0.05	0.01
Cu	0.01	0.01	0.01	0.01
Cd	0.10	0.18	0.17	0.08
Zn	0.15	0.12	0.02	0.01

Table 4.5 Heavy metal concentrations (mg/l) from Site 5 (Teluk Intan)

Heavy Metal	Depth (m)			
	(0 - 10)	(10 - 20)	(20 - 30)	(30 - 40)
Ca	1.76	12.76	25.63	-
Pb	1.14	3.76	13.19	-
Ni	0.04	0.58	0.36	-
Fe	1.17	196.42	13.92	-
Mn	0.01	88.55	0.01	-
Cu	0.01	0.12	0.72	-
Cd	0.22	2.22	4.07	-

Zn	0.24	0.45	2.35	-

Chemical analysis was not carried out when insufficient or very little water was collected. Hence at some sites, results of heavy metal concentrations at the 30-40 m depth interval is not presented.

From the results listed in the above tables, several distinct features can be distinguished:

1) Calcium content of the interstitial water is generally quite high and is comparable to the calcium concentration in limestone groundwater which has been reported to be averaging 51.3 mg/l (Crowther, 1989).

2) The lowest Ca content in interstitial water was detected at the Teluk Intan site between 0-10 m in depth.

3) High Zn content, greater than 110 mg/l between 10 to 20 m depth interval at Site 1.

4) Only at the Sabak Bernam landfill, Site 1 and Teluk Intan sites which show the Fe content greater than 1 mg/l. The Sabak Bernam landfill contains between 5 to 10 mg/l of Fe at depth intervals of 0-10 m and 10-20 m. At Site 1, Fe content is highest at 20-30 m depth interval and amounts to about 11 mg/l. At a depth interval between 10 to 20 m, the Fe content in the interstitial water at Teluk Intan site reaches a value of almost 200 mg/l.

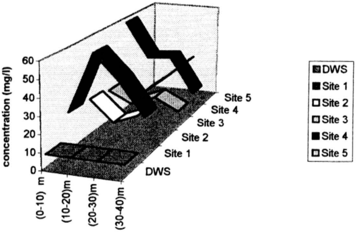
5) Mn^{2+} ions are also in abundance in interstitial water at depth interval between 10-20 m at the Teluk Intan site. About 89 mg/l of Mn was detected.

In the forthcoming sections these distinguished features will be discussed in more detail, element by element, so as to gain some understanding on its distribution with respect to the soil properties and probably the anthropogenic activities at the various sites of study.

Calcium

Overall the calcium content obtained is greater than the limit permissible in domestic water supply (DWS) i.e. 7.5 mg/l (Tong, 1997; see Appendix B) except for the Ca content obtained at the depth interval between 0-10 m at Teluk Intan.

Fig.4.1 Calcium distribution by site and depth



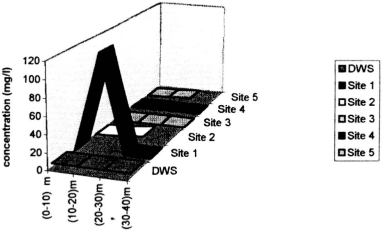
The lithographic strata of Malacca (Mohd Nazan Awang et al., 1992) is quite similar to the sites involved in the present study i.e. comprising alluvial soil. It was found that the

Ca^{2+} content in the soil strata of Malacca (from the more than 100 mukims studied) is quite high in only two mukims i.e. 176 ppm and 220 ppm while in most of the mukims the concentration of Ca^{2+} was quite low. Hj Saffen Baharuddin (1992) reported a series of experiments with the alluvium soil of Kuantan and Pekan. The results showed that the Ca^{2+} contents in 9 bore hole areas out of 21 holes were more than 7.5 mg/l which is also above the permissible limit for domestic consumption and the Ca^{2+} content for all wells in the study was in the range between 1.3 to 78 mg/l. The results of Ca^{2+} content in this study ranged between 1.84 to 57.8 mg/l.

Zinc

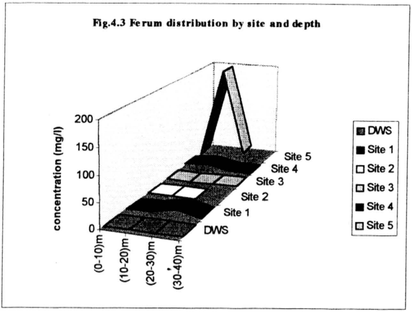
Figure 4.2 shows the zinc distribution at all depths of investigation from all sites of study. Zn pollution is closely related to the type of industrial activity (Perin et al., 1997). In the Port Klang area, there are several small scale steel industry near Bukit Raja and petrochemical industry near Pandamaran Industrial Area which is nearer the present site of study and therefore the zinc content is high in this area. On the whole Zn pollution is not severe in other sites and mainly below the limit (5 mg/l) imposed for DWS.

Fig.4.2 Zinc distribution by site and depth



Ferum

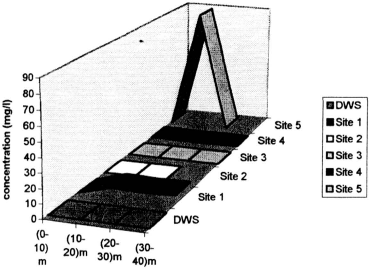
Figure 4.3 shows the ferum distribution. The highest concentration was found in the Teluk Intan area (196.42 mg/l). According to Pyeong et al., (1997), iron complexes well with organic matter. From a report by Cadence Kontrak Bina Sdn. Bhd. (1998), the amount of organic matter in the soil content is highest at this depth level, 51.2%. The next site with a high Fe content is Port Klang which can be attributed to the small scale steel industry. The permissible Fe limit in water for domestic use is 0.1 mg/l and this is half of the permissible value, for drinking water quoted by Al-Tabbaa et al., (1997) for United Kingdom.



Manganese

Figure 4.4 shows the Mn distribution. The Teluk Intan interstitial water again dominates the Mn content and is found in abundance with Fe at the same depth interval. This observation shows that there is some association between the movement of one metal with other metals in the interstitial water. Pyeong et al.,(1997) have calculated the distribution coeffient of several heavy metals such as Pb, Zn, Cd and Mn in gram per liter. As to the abundance of Mn at 10-20 m depth intervals, Pyeong et al., (1997) have explained that this could be attributed to the upward migration of Mn $^{2+}$ which could possibly have occurred from buried sediments in the soil and their subsequent accumulation at the sediment-water interface due to the precipitates of Mn^{4+} oxides or the incorporation of Mn in Fe hydroxides. Perin et al., (1997) have also reported similar relationship among metal distribution in water. The permissible limit for Mn in domestic water supply is 0.05 mg/l. Only the Sg. Lang interstitial water is not contaminated with Mn.

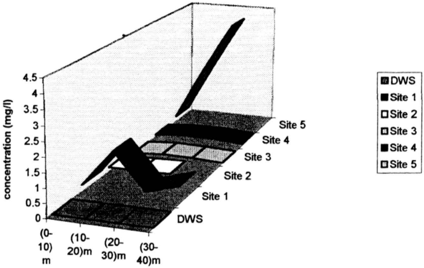
Fig.4.4 Manganese distribution by site and depth



Cadmium

The Cd distribution in interstitial water for the various sites are given in Fig. 4.5. The abundance of Cd can be observed in interstitial water from the Teluk Intan and Port Klang sites. Cd is potentially toxic to both human and animals and it is therefore desirable to minimise the amount of Cd in foodstuffs (Loganathan and Hedley, 1997). Most Cd applied to undisturbed soil remains in the top few centimeters of the soil where the active plant roots are, and it is considered to move very slowly down the soil profile. It is generally believed that Cd is unlikely to pollute water or even interstitial water because of its low mobility in soils.

Fig.4.5 Cadmium distribution by site and depth



Mann and Ritchie (1995) suggested that there is a greater risk of Cd being leached into the ground and interstitial water in sandy soils. Reference to the report by Cadence Kontrak Bina Sdn. Bhd. (1998) for the soil type at the Teluk Intan and Port Klang sites showed that at the depth of 24 m the lithographic unit of the site at Teluk Intan is sandy (>60%) and at a depth of 30 m the lithographic unit is greater than 90% sandy. This accounts for the high Cd concentration in the interstitial water at depth intervals 20-30 m and 30-40 m at the Teluk Intan site. At the Port Klang area along the depth interval where

Cd concentration was found to be 1.55 mg/l, the soil also consists of sand (~20%). It is to be noted that the highest Cd concentration is slightly more than 4 mg/l implying that Cd leaching mobility is also quite low. Domestic water supply should not exceed 0.005 mg/l in its Cd content. Hence, based on the results obtained, the Cd concentration is too high for the water to be used for human consumption. Mench et al., (1997) has reported that the total Cd content in soil is not significantly related to the Cd concentration in edible plant parts; again implying its low mobility.

Lead

Lead is found in abundance at the Teluk Intan site (~ 4 mg/l) and Figure 4.6 illustrates the Pb distribution in all areas of investigation. Pb is a naturally occurring heavy metal that has been widely used. The major environmental sources of metallic lead are paint, water, food and autoexhaust (Ho and Ho, 1997). The most important lead accumulating pathways are through lead inhalation from automobile emission, drinking water and food from lead-soldered cans and plumbing. Ingestion of chips from lead-painted surfaces is also common among children. Lead can be deposited on and retained by crops, particularly leafy vegetation. Inorganic lead, which enters the body primarily through ingestion and inhalation does not undergo biologic transformation, while organic lead is metabolised in the liver. Organic lead is found primarily in gasoline as tetraethyl lead, which is a serious environmental hazard. Inhaled lead deposited in the lower respiratory tract is completely absorbed. For pregnant women and children ,the amount absorbed can increase to as much as 50%. Lead is distributed primarily among blood, soft tissue, bones and teeth. Bones and teeth contain about 95 % of the total body burden of lead in adults. When the body is under physiologic stress such as pregnancy and lactation, the blood lead level increases. The high lead content in Teluk Intan could be due to grill making, which makes use of solders containing lead, boat repairing and agricultural activities. For DWS, lead content should not exceed 0.05 mg/l. Once again the results obtained shows that the amount of lead in the interstitial water makes it unsuitable for human consumption.

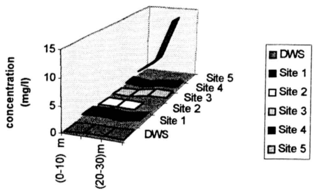
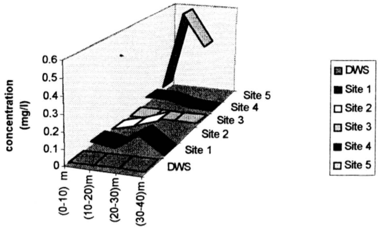


Fig.4.6 Lead distribution by site and depth

Nickel

Figure 4.7 depicts the nickel distribution. The high nickel concentration at Teluk Intan site compared to other sites could be attributed to steel-related industries as have been shown by Teixeira,et all (1997). Ni limit in domestic water supply is 0.011 mg/l. The results obtained on the present investigation indicate that only site 3 (Sg. Lang) has trace levels of Ni (about that permissible for DWS) but site 5 (Teluk Intan) has very high Ni content (~0.5 mg/l).

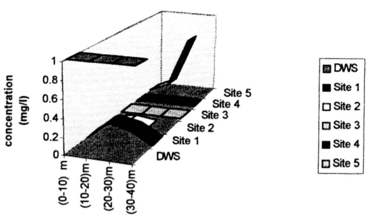
Fig.4.7 Nickel distribution by site and depth



Copper

Figure 4.8 illustrates the copper distribution in interstitial water. The highest Cu content in the interstitial water is only 0.7 mg/l and is below the permissible level for domestic consumption. Copper is toxic to zooplanktons, algae and larval stages of marine invertebrates (Breslin Adler-Ivanbrook, 1998). Cu^{2t} is the most toxic form of copper but there is also evidence for toxicity for both the free and complexed forms of copper. The copper limit for DWS is 1 mg/l. From the results obtained, the interstitial water collected from all sites are not contaminated by Cu.

Fig.4.8 Copper distribution by site and depth



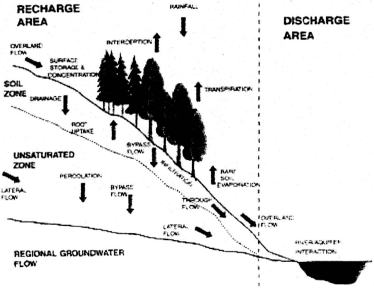


Figure 4.9 Concept of water balance.

In general, since the heavy metals are dissolved in the interstitial water, any factors that influence interstitial water will also affect the heavy metal distribution. The amount of interstitial water is therefore also influenced by the recharge processes as show in Figure 4.9.

The processes can be grouped into (i) the surface/atmosphere zone and (ii) the soil zone and the unsaturated zone. Processes occurring in zone (i) include interception of precipitation by the vegetation canopy as well as evaporation and transpiration. Surface runoff may occur and resulting in (a) concentration through ponding and (b) gains and losses from overland flow.

The soil zone encompasses drainage to the underlying zone and root uptake, both upward and downward water movements can occur in this zone. Therefore it is not the same as the soil zone defined by soil scientists (Finch et al., 1997), but can be taken to extend from the surface down to a depth below which no upward movement of water ever occurs. This implies that the thickness of the zone is a function of both the soil/rock properties and the rooting depth of vegetation. Lateral flow through the soil layer can also result in gains and losses of water. Thus due to these gains and losses of water, the concentrations of heavy metal in the interstitial water obtained from all locations in this study are observed to fluctuate at different depth intervals. The depth interval of 10 m was taken in this study to obtain sufficient water for analysis. A plausible reason to the high heavy metal content in the interstitial water in general could probably be due to in situ heavy metals leaching out of the soil into the interstitial water when the soil was squeezed during collection.

4.3 Heavy metal distribution in landfill at Sabak Bernam

Thus far, discussion pertains to the various sites which are not landfill areas nor are they areas where waste materials are deposited. One of the chosen study sites is a landfill area (Site 4,) in Sabak Bernam. Economic consideration continue to keep landfills as the most attractive disposal route of municipal solid waste. The great majority of solid waste generated world-wide (residential, commercial and industrial) is correctly disposed of in landfills.

Despite the evolution of landfill technology from open, uncontrolled dumps to highly engineered facilities designed to eliminate or minimise potential adverse impacts of the waste on the surrounding environment, generation of contaminated leachate remains an inevitable consequence of the practice of waste disposal in landfill. The subsequent migration of leachate away from landfill boundaries and the release to the adjacent environment is a serious environmental pollution concern and threat to public health and safety at both old and new facilities. Groundwater pollution is by far the most significant concern arising from leachate migration (El-Fadel et al., 1997). Once leachate reaches the bottom of a landfill or an impermeable layer within the landfill, it travels laterally either to a point where it discharges to the ground surface as a seep, or it moves into the landfill and into the substrate formations. Depending upon the nature of these formations and in the absence of a leachate collection system, leachate has been associated with the contamination of aquifers underlying landfills. The high Ca content in the interstitial water could be attributed to the biomass from agricultural activities (Ghestem and Bermond, 1998). This can be observed from the accompanying photograph, Figure 4.10.

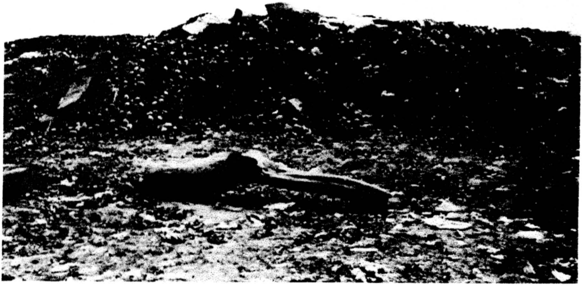
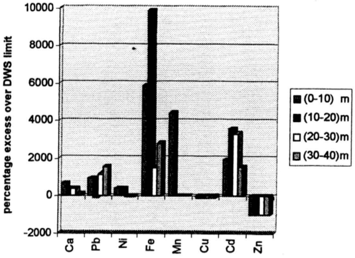


Fig.4.10 Landfill used to discard agricultural wastes. Picture taken at Sabak Bernam landfill.

On the whole, the distribution of heavy metals can be observed to be influenced by the lateral movement of leachate into the bore hole area dug at the site. Only Cu and Zn concentrations are below that accepted for domestic purposes. Figure 4.11 illustrates, the percentage excess of the heavy metals in the interstitial water with reference to the permissible limit for each metal in DWS.

Fig. 4.11 Percentage excess of elements in interstitial water from landfill



Once again, it can be observed that there seem to be some relationship between the movement of Fe and Mn in the interstitial water obtained from the landfill site. The low Mn concentration at depth intervals greater than 10 m could be due to Mn being incorporated in Fe hydroxides. The Fe content in the leachate is greater than 1000 % in excess of the permissible limit for DWS. Other heavy metals such as Pb and Cd are also greater than 1000 % in excess of their permissible limits. These could be attributable to the corrosion processes of metal wastes through which lead and ferum were discharged. Since Sabak Bernam is also an agricultural area, the elevated levels of Pb and Cd could also be attributed to the application of agrochemicals, pesticides, animal manures and fertilisers as suggested by Chen et al., (1997).

4.4 Soil moisture content

Table 4.6 lists the moisture content of the soil dug at the Sg. Lang (Site 3).

Table 4.6 Moisture Content in Percentages at Sg. Lang. (Site 3)

Depth (m)	Weight			moisture content (%)
	m_1 (g)	m_2 (g)	m_3 (g)	
0-10	12.5	37.7	25.5	92
10-20	12.2	40.7	29.4	66
20-30	11.6	44.8	29.5	85
30-40	12.3	30.6	22.4	80

Table 4.7 lists the moisture content at the various depth intervals for the landfill site (Site 4).

Table 4.7 Moisture content in percentages at Landfill.

Depth (m)	Weight			moisture content (%)
	m_1 (g)	m_2 (g)	m_3 (g)	
0-10	12.6	41.0	24.0	150
10-20	12.0	42.0	27.0	121
20-30	12.5	39.2	26.3	93

30-40	11.7	38.5	25.9	87

4.5 pH of soil

Variation of soil pH with depth at the Sg. Lang site is depicted in Figure 4.12.

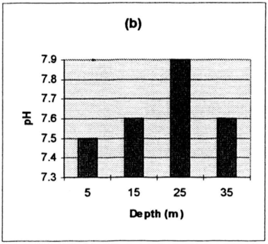


Fig. 4.12 Soil pH for Site 3

Figure 4.13 depicts the soil pH with depth at the Landfill site.

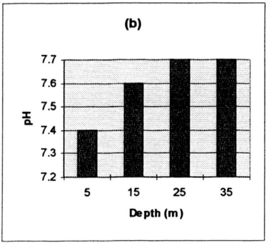


Fig.4.13 Soil pH at Site 4.

4.6 Influence of soil pH and soil moisture on heavy metal distribution

It was observed that some kind of "loose" qualitative relationship on the existence of some heavy metals in interstitial water. From observations made in the present study, it may be possible to infer that the existence of one of the elements could imply the possible existence of the other element. This is true to some extent for Fe and Mn in at least two locations, i.e. at Site 5 (Teluk Intan) and at Site 4 (landfill). In this section, investigation is narrowed down to two sites in the same district of Sabak Bernam i.e. Site 3 and 4, in order to study the effect of soil moisture and pH on the distribution of heavy metals in the interstitial waters obtained.

Sg. Lang (Site 3)

Figure 4.14 compares the moisture, pH and heavy metal distribution with depth into the ground in order to discuss the influence of moisture and pH on the distribution of each heavy metal with depth.

The calcium distribution is more moisture dependent rather than pH. This is based on the observation that the trend of moisture variation with depth of investigation is quite similar to the trend of Ca concentration with depth of investigation.

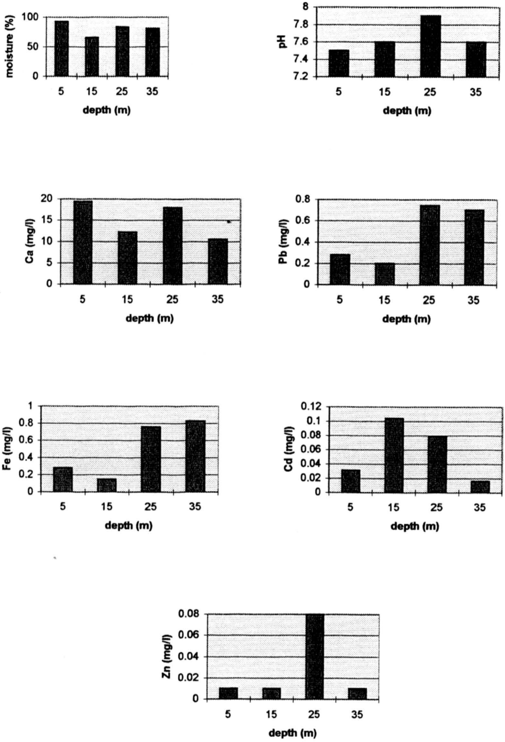


Fig. 4.14 Comparison between moisture, pH and heavy metal distribution at Site 3 (Sg. Lang).

The Pb distribution could be sensitive to both moisture and pH, since the variation in moisture and pH with depth from 15 m to 35 m is almost similar to the variation in Pb content for the same depth intervals. However, since the Pb^{2+} ions are dissolved in interstitial water, lateral discharge of water at this depth may be the factor responsible for the low Pb content at depth interval 10-20 m. To support this reasoning, for the same depth interval, of which the mean is plotted on the graph, there is a decrease in moisture content, implying about the possible loss of water through lateral movement in the ground.

The trend in moisture - depth variation is quite similar to that of the Fe concentration variation with depth. However, the profile of the Fe content has a much deeper valley than the profile of the moisture content. The decrease in moisture content at 15 m (in the 10-20 m range is accompanied by a decrease in the Fe content in interstitial water. Likewise, an increase in Fe content at 25 m is accompanied by an increase in moisture content. However, there could still be other factors influencing the Fe distribution because there is a slight increase in Fe content at 35 m which is accompanied by a slight decrease in moisture content. Recharge of interstitial water could not be an attributing factor since this would result in the increase in moisture content and probably because the Fe content due to additional leaching of ferum into the soil, but results show otherwise. So recharge of interstitial water at this depth could not be used as a plausible explanation.

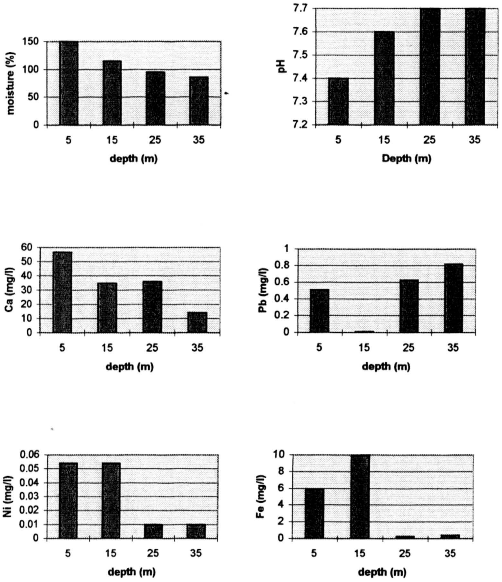
From the results obtained, there could be some correlation between the Cd distribution with pH since the Cd content seem to increase with pH at depths of 5 m and 15 m. However at 25 m the pH of the soil is much higher and this is accompanied by a decrease in Cd concentration. The Cd concentration could not be influenced by moisture since the Cd concentration-depth variation for 5 to 35 m is in the opposite direction to that of the moisture distribution for the same depth intervals. The correlation between pH and Cd content is once again observed at 30-40 m depth interval.

The influence of pH on Zn distribution is quite strong as the pH-depth variation can be said to be similar to the zinc concentration-depth profile except for the lower Zn content at 15 m which could be attributable to the loss of water through lateral movement or downward movement to the 25 m depth. The lower moisture content at 15 m could be the only role played by moisture in influencing the Zn distribution with depth of investigation. The influence of pH and moisture on the distribution of Ni, Mn and Cu are not discussed due to their low concentration in the interstitial water obtained from Sg. Lang.

From this investigation, it can be inferred that the Cd and Zn distribution are pH dependent. Fe and Ca distributions are moisture dependent. The distribution of Pb could be governed by pH and moisture.

Landfill (Site 4)

Figure 4.15 illustrates the moisture, pH and heavy metal distributions at Site 4 (landfill).



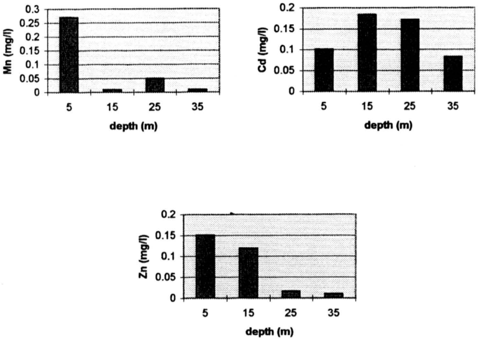


Fig.4.15 Comparison between moisture, pH and heavy metal distribution at Site 4 (landfill).

As mentioned for the Ca content distribution with depth into the soil for the interstitial water obtained from Sg. Lang, again it can be observed that the Ca distribution with depth for the interstitial water obtained from Site 4, Fig.4.15 is moisture dependent. On the other hand, pH could possibly influence the Pb distribution in the interstitial water collected at Site 4. This observation is in reasonable agreement to the results of Sauve et al., (1997). However, the almost zero concentration at 15 m could be due to loss of water as indicative of the decrease in moisture content. However, the pH factor is much stronger than the moisture factor since the highest Pb content is at 35 m where pH of the soil is also highest.

The Ni distribution does not seem to be influenced by pH but could be governed to some extent by the moisture content of the soil. This is because the trend of Ni concentration variation with depth is quite like that of moisture variation with depth. The Fe distribution may be moisture dependent. This inference is supported to some extent by the fall in moisture content of the soil. The rise in Fe content at 10-20 m depth interval could be attributable to the leaching of Fe into the soil from lower depths where the pH is higher. After arriving at the new depth (15 m), Fe is not easily leached into the soil. This could be due to the increase in alkalinity of the soil. At greater depths, since Fe is not easily 'extractable' in alkaline medium (Yousfi and Bermond, 1997). Thus the Fe remains *in situ* in the soil and the Fe content at 20-30 m and 30-40 m depth intervals is very low.

The Mn and Cd distributions are moisture controlled and this can be inferred from the trends of their depth profiles with the moisture profile. From the Zn-depth profile, it can be observed that moisture influences the distribution of Zn concentration with depth into the soil. This is because the Zn concentration-depth profile and the moisture-depth profile is similar. However, the rate of water loss could be another influencing factor since the Zn content is quite low at 25 m and 35 m. Also Zn could be adsorbed on Mn/Fe-oxy-hydroxides co-precipitation, forming a franklinite-type double oxide after $Zn^{2+} + 2Fe^{3+} + 4H_2O \rightarrow ZnFe_2O_4 + 8H^+$ (Perin et al., 1997) leaving a lower concentration of Zn^{2+} to be detected in this work.

Moisture and pH influences the heavy metal distribution in interstitial water from Site 4 in almost the same way as the influence on heavy metal distribution in interstitial water from Site 3. However, the nickel distribution is moisture controlled at the landfill site and the manganese distribution is governed by pH. Both manganese and nickel are of very low concentration in the interstitial water of Sg. Lang. Copper is present in trace amounts in the interstitial waters at both sites.

In short, pH and moisture do affect the existence of elements to some extent. Other factors such as lateral recharge and discharge of water can come into play. The alkaline nature of the soil could be attributed to the high concentration of calcium which could have neutralised the soil's acidity. Moreover, the ferum content is quite low in Sites 3 and 4. According to van Tonder and Schutte (1997), calcium (which may exist as a hydroxide) neutralization of acidity is impaired by ferum. Since the ferum content is quite low compared to the calcium content, the presence of calcium in interstitial water could have made the soil neutral or slightly alkaline.