A Study on Physico-Chemical analysis of Ground Water and Heavy Metal Analysis of Leachate in Kodungaiyur Landfill Site, Chennai

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Abstract: The Leachate heavy metal samples were analysed for its Physico-Chemical and Heavy metal characteristics to assess a pollution level in soil condition of kodungaiyur dumping yard. Water quality analyses were carried out for its suitability of drinking water condition and compare the result with WHO and BIS standards. Investigation on the accumulation heavy metals like Fe, Pb, Zn, Cu, Cd and Cr in leachate as per APHA methods are carried out. In leachate, the order was Pb>Zn>Cu>Cr>Cd.

Keywords: Heavy Metals, Geo-chemical Index, Enrichment Factor, Contamination Factor, Leachate, Dumping Yard.

Introduction

The accumulation of heavy metals and metalloids in environment is of increasing concern now a day. Potentially harmful metal in nature may come from the bedrock itself and anthropogenic sources like solid and liquid waste deposits from various sources like domestic, industry, agricultural and transport emission etc., (Wilson and Pyatt, 2007). Excessive accumulation of heavy metals in nature results in ground water pollution, soil contamination and has consequences for health effects on living beings and agriculture failure. MSW generated in Chennai includes 68 % of residential waste, 16 % commercial waste, 14% Institutional waste and 2 % industrial waste. The Physico-chemical properties of the MSW generated in Chennai, showed that the majority of the waste is composed of green waste (32.3%) and inert materials (34.7%) viz., stones and glass (CPCB, 2000 and Damodaran et.al., 2003).
Study Area

The Kodungaiyur dumping yard located at the northern part of Chennai city is in operation since 1980. It comes under Perambur Taluk of Chennai City District. Initially the leachate generated from the Chennai city has been dumped in Kodungaiyur dumpsite. Due to urbanization, increase in population, changes in lifestyle and consumption pattern, the problem of water waste management in Chennai has increased. So two other major, Perungudi in south and Kodungaiyur in north have been proposed and being used as open dumps for disposal of Municipal Water Waste from the Chennai city. Now Kodungaiyur has been used as a dumping ground for municipal waste since 1987. Latitude and longitude of kodungaiyur will be 13° 08’ 02” N and 80° 16’ 09” E. Elevation of 7 meter above mean sea level. The method of disposal is open dumping and levelling by bulldozer.

The dumping site covered about 30 ha in 1995 and increased to 54.75 ha in 2002 which is twice that of the area in 1995. The dumping area is estimated to be 117 ha in 2009 which is again twice as that of in 2002. Kodungaiyur sewage water treatment plant located adjacent to the dumpsite discharges the sewage water near to the dumpsite. The waste at the site mixes with the sewage water and contaminates it further. The dumpsite lies at 1.5 to 2.0 km from the western side of Buckingham canal and 3 km west of Bay of Bengal coastline. It is situated within a low lying IOC marsh which extends for a length of approximately 10 km from north to south and for a width of 3 to 4 km from west to east that makes the dumpsite always surrounded by water courses. Many industries in and around kodungaiyur such as Madras Fertilizer Limited (MFL), Indian Oil Corporation (IOC), and Madras Refinery Limited (MRL), etc., It is said to be the largest dump yard in Chennai city maintained by Chennai Corporation. It has many harmful effects on residents in the vicinity to the dump yard, in violation of MSW Rules framed by Ministry of Environment and Forests and Climate Change.

The monthly average weather statistics of Kodungaiyur are as follows:

| S.No | Months   | Temperature | Precipitation |
|------|----------|-------------|---------------|
|      |          | Normal      | Warmest       | Coldest       | Normal    |
| 1    | January  | 24.6°C      | 28.8°C        | 20.4°C        | 1         |
| 2    | February | 26.2°C      | 30.7°C        | 21.6°C        | 1         |
| 3    | March    | 28.4°C      | 33.2°C        | 23.5°C        | 0         |
| 4    | April    | 30.9°C      | 35.6°C        | 26.2°C        | 1         |
| 5    | May      | 32.9°C      | 38.0°C        | 27.7°C        | 2         |
| 6    | June     | 32.4°C      | 37.4°C        | 27.4°C        | 7         |
| 7    | July     | 30.7°C      | 35.3°C        | 26.0°C        | 9         |
| 8    | August   | 30.1°C      | 34.5°C        | 25.6°C        | 10        |
| 9    | September| 29.7°C      | 34.0°C        | 25.3°C        | 10        |
| 10   | October  | 28.2°C      | 31.9°C        | 24.4°C        | 12        |
| 11   | November | 26.1°C      | 29.5°C        | 22.7°C        | 11        |
| 12   | December | 25.0°C      | 28.4°C        | 21.5°C        | 6         |

Source: Madras/Minambakkam weather station: 16 m.a.s.l., 16.0 km away from Kodungaiyur.

Sampling and Methodology

This study collected six leachate samples and ground water samples from the buffer zones of landfill site at the distance interval of 200m to identify the variations in quality of samples. The site is under marshy land, 3 to 4 km away from coastline of Bay of Bengal. The study area experiences tropical climate and features fairly hot most of the months. According to Minambakkam weather station in Chennai recorded the normal maximum and minimum temperatures are 32.9°C (May) and 24.6°C (January) respectively. The samples were collected in a pre-cleaned one litter polyethylene sample
container. The container was washed with detergent and soaked with 1% nitric acid. Then sample containers were rinsed with deionised water. For measuring heavy metal concentration, 65% concentrated HNO$_3$ acid was added to each sample immediately after the collection to bring the pH below 2 to minimize precipitation and adsorption in the container walls (APHA 1998).

**Table 2**

| Parameter | Instrument Used | Method Used | Method Reference |
|-----------|----------------|-------------|------------------|
| pH        | Digital pH meter | -           | APHA (1998)      |
| EC        | Digital Conductivity Meter | -           | Trivedi and Goel (1986) |
| TDS       | TDS Meter       | Evaporation |                  |
| COD       | Refluxing Assembly | Reflushititrmetry method | APHA (1998) |
| BOD       | BOD incubator and titration assembly | Winkler azide method | APHA (1998) |
| Na$^+$    | Flame photometer | Calibration | Flame atomic absorption spectrometer (FAAS) |
| K$^+$     | Flame photometer | Calibration |      |
| Cl$^{-}$  | Burette         | Titration   | APHA (1998)      |
| NO$_3^-$  | UV-Spectrometer |            |                  |
| Elements  | Atomic Absorption Spectrometer |            |                  |

**Assessment of Metal Contamination**

In order to assess the heavy metal contamination in the landfill site of the study area. Three quantitative indices namely: Geo-accumulation Index (Igeo), Enrichment Factor (EF) and Heavy Metal Pollution Index (HPI) were utilised.

**Geo-accumulation Index**

The geo-accumulation Index is used to evaluate the accumulation of contamination in sediments (Muller, 1969). It is defined as:

$$I_{geo} = \log \frac{C_n}{1.5B_n}$$

Where,

- $C_n$ – Measured Concentration of Element;
- $B_n$ – Geo-chemical Background Value;
- 1.5 – Constant;

The constant 1.5 allowed to predicting the possible natural fluctuations in background data due to litho-logic effect.

**Table 3** Concentration of heavy metals in world surface rock average.

| Elements | World Surface Rock Average in ppm | Indian River Sediment in ppm | Undisturbed Sediment Value |
|----------|----------------------------------|------------------------------|-----------------------------|
| Fe       | 35900                            | 29000                        | 46000                       |
| Pb       | 16                               | -                            | 20                          |
| Zn       | 127                              | 16                           | 95                          |
| Cu       | 32                               | 28                           | 45                          |
| Cd       | 90                               | -                            | 0.3                         |
| Cr       | 71                               | 87                           | 90                          |

Source: Martin Meybeck (1979), Subramaniam et al (1987), Turekian and Wedepohl (1961). Values are in ppm.

**Table 4** The seven grades or classes of profile of the Geo-Accumulation Index proposed by Muller (1981).

| S.No | Sediment Accumulation Index ($I_{geo}$) | $I_{geo}$ Class | Pollution Intensity       |
|------|---------------------------------------|-----------------|---------------------------|
| 1    | >5                                    | 6               | Very Strong Pollution     |
| 2    | >4-5                                  | 5               | Strong to Very Strong     |
Enrichment Factor/ Contamination Factor (EF)

The enrichment factor is a measure to differentiate the sources of heavy metals between lithogenic and naturally occurring Iron (Fe) to normalize the heavy metal distribution (Rule 1986; Naji and Ismail, 2011). The Enrichment factor for Fe-normalization is defined by:

$$EF = \frac{(M_x / Fe_x)}{(M_c / Fe_c)}$$

Where:
- $M_x$ – Concentration of heavy metals in sourced sample
- $M_c$ – Concentration of heavy metals in Undisturbed Sediments;
- $Fe_x$ - Concentration of Fe in Spotted Samples;
- $Fe_c$ - Concentration of Fe in Average Undisturbed Sediments;

The average shale values used in this study were tabulated in Table No:

| EF Range | Assessment Category       | Result                          |
|----------|---------------------------|---------------------------------|
| < 1      | I                         | No Enrichment                   |
| 1-2.9    | II                        | Minor Enrichment                |
| 3-4.9    | III                       | Moderate Enrichment             |
| 5-9.9    | IV                        | Moderately Severe Enrichment    |
| 10-24.9  | V                         | Severe Enrichment               |
| 25-49.9  | VI                        | Very Severe Enrichment          |
| >50      | VII                       | Extremely Very Severe Enrichment |

Contamination Factor

The level of contamination of sediment by heavy metal is expressed in terms of contamination factor (CF) calculated as

$$Contamination \ Factor \ (CF) = \frac{S_{sample}}{C_{Background}}$$

Where, $S_{sample}$ – Concentration of the given metal in River Sediment.
- $C_{Background}$ – Concentration Value of the metal equals to the world surface rock average.

| Contamination Factor | Classification            |
|----------------------|---------------------------|
| < 1                  | Low Contamination         |
| 1 < CF < 3           | Moderate Contamination    |
| 1 < CF < 3           | Considerable Contamination|
| CF > 6               | Very High Contamination   |

Heavy Metal Pollution Load Index

Heavy metal pollution index (HPI) is a method of rating that shows the composite influence of individual heavy metal on the overall quality of water. It is used to evaluate overall pollution with respect to heavy metals (Prasad B, Kumari S, 2008). Pollution Load Index of particular site can be estimated using the method proposed by Tomilson et al. (1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$
Where CF is the contamination Factor and n is the no of metals.

Results and Discussion

Leachate pH level: Leachate is generally found to have pH between 4.5 and 9 (T. H. Christensen, P. Kjeldsen, and P. Kjeldse, 2001). The pH of young leachate is less than 6.5 while old landfill leachate has pH higher than 7.5 (A. A. Abbas, G. Jingsong et al, 2009). Initial low pH is due to high concentration of volatile fatty acids (VFAs) (J. Bohdziewicz and A. Kwarciak, ). Stabilized leachate shows fairly constant pH with little variations and it may range between 7.5 and 9.

Physio-chemical characteristics of the leachate depend primarily upon the waste composition, depth of waste, moisture content, available oxygen, temperature, co-disposal with inclinator ash, waste processing, age of landfill, toxicity and water content in total waste. The characteristics of the leachate samples collected from the dumpsite has been presented in Table 7. Variation in the conductivity was very high (2360μmhos/cm) and is the main indicator of dissolved inorganic species or total concentration of ions. Though the pH values were within the stipulated standards, the levels can be used to explain the nature of the leachate. Higher pH (> 8) value indicates the alkaline nature of leachate. This shows that the biochemical activity in the landfill was in its final stage and the organic load was biologically stabilized. During the initial stage or acetogenic stage, the pH values are quite low (<7). The maximum pH value of leachate at dumpsite is 7.68. The presence of high BOD (20282 mg/l) and COD (27621 mg/l) indicates high organic strength of leachate. In all six leachate samples sample-1 shows the high value of ammonia nitrogen (2251 mg/l) indicates the decomposition of organic matter. The high TDS value of 28512 mg/l shows presence of inorganic material in the leachate sample.

Table 7 Physico-Chemical and Heavy metal characteristics of Leachate at landfill sites

| S.No | Parameter | L = 200 m | L = 400m | L = 600m | L = 800m | L = 1000m | L = 1200m |
|------|-----------|-----------|----------|----------|----------|-----------|-----------|
| 1    | pH        | 7.68      | 7.33     | 7.13     | 7.10     | 7.04      | 6.93      |
| 2    | EC        | 2596.00   | 2478.00  | 2436.48  | 2419.98  | 2397.15   | 2368.80   |
| 3    | TDS       | 28512.00  | 27216.00 | 2426.76  | 24577.16 | 24345.30  | 2359.35   |
| 4    | COD       | 27621.00  | 26365.50 | 2504.80  | 25712.88 | 24935.40  | 26103.00  |
| 5    | BOD       | 20282.90  | 19360.95 | 17695.80 | 17564.2  | 17298.5   | 17204.25  |
| 6    | Na+       | 741.40    | 707.70   | 597.24   | 571.34   | 565.95    | 580.65    |
| 7    | K+        | 1393.70   | 1330.35  | 1245.24  | 1193.56  | 1182.30   | 1210.65   |
| 8    | NH4+      | 2251.70   | 2149.35  | 1888.92  | 2058.52  | 2039.10   | 1836.45   |
| 9    | NO3       | 433.40    | 413.70   | 368.28   | 395.38   | 391.65    | 358.05    |
| 10   | Fe        | 85.80     | 81.90    | 70.20    | 64.66    | 64.05     | 68.25     |
| 11   | Pb        | 1.33      | 1.27     | 1.38     | 1.38     | 1.37      | 1.34      |
| 12   | Zn        | 2.20      | 2.10     | 1.80     | 1.80     | 1.79      | 1.75      |
| 13   | Cu        | 0.86      | 0.82     | 0.68     | 0.73     | 0.72      | 0.66      |
| 14   | Cd        | 0.04      | 0.04     | 0.03     | 0.03     | 0.03      | 0.03      |
| 15   | Cr        | 0.42      | 0.40     | 0.38     | 0.35     | 0.35      | 0.37      |
Table. 8 Statistical Analysis of Leachate Characteristics

| Para    | Min   | Max   | Average | Median | SD    | Kurtosis | Skewness | Variance |
|---------|-------|-------|---------|--------|-------|----------|----------|----------|
| pH      | 6.93  | 7.68  | 7.20    | 7.12   | 0.33  | 1.11     | 0.36     | 0.07     |
| EC      | 2368.8| 2596  | 2449    | 2428   | 102.50| 1.43     | 0.19     | 6513     |
| TDS     | 2359.35| 28512 | 12813   | 24461  | 9651.64| 5.16     | -2.22    | 153154089|
| COD     | 24935.4| 27621 | 26174   | 25769  | 1420.24| -0.98    | -0.17    | 1025449  |
| BOD     | 1739.85| 20283 | 13006   | 9726   | 9563.97| -3.25    | 0.03     | 77287474 |
| Na+     | 565.95| 741.4 | 627     | 584    | 83.42 | -1.47    | 0.83     | 5891     |
| K+      | 1182.3| 1393.7| 1259    | 1219   | 100.13| -0.93    | 0.54     | 7185     |
| NH4+    | 1836.45| 2251.7| 2037    | 2048   | 132.82| -0.63    | 0.31     | 24266    |
| NO3     | 358.05| 433.4 | 393     | 393    | 24.61 | -0.65    | 0.51     | 779      |
| Fe      | 64.05 | 85.8  | 72      | 67     | 10.26 | -1.64    | 0.70     | 84       |
| Pb      | 1.27  | 1.38  | 1.35    | 1.35   | 0.05  | -1.40    | -0.59    | 0.00     |
| Zn      | 1.75  | 2.2   | 1.91    | 1.80   | 0.20  | -1.19    | 0.91     | 0.04     |
| Cu      | 0.66  | 0.86  | 0.75    | 0.73   | 0.07  | -1.19    | 0.78     | 0.01     |
| Cd      | 0.03  | 0.04  | 0.04    | 0.03   | 0.01  | -1.58    | 0.94     | 0.00     |
| Cr      | 0.35  | 0.42  | 0.38    | 0.36   | 0.03  | -1.51    | 0.36     | 0.00     |

Table. 9 Results of Geo chemical Index

| S.No | Fe  | Pb   | Zn   | Cu  | Cd  | Cr  | Result                  |
|------|-----|------|------|-----|-----|-----|-------------------------|
| S1   | -9.29| -4.17| -6.44| -5.80| -11.72| -7.99| Cd > Fe > Cr > Zn > Cu > Pb |
| S2   | -9.36| -4.24| -6.50| -5.87| -11.72| -8.06| Cd > Fe > Cr > Zn > Cu > Pb |
| S3   | -9.58| -4.12| -6.73| -6.14| -12.14| -8.13| Cd > Fe > Cr > Zn > Cu > Pb |
| S4   | -9.70| -4.12| -6.73| -6.04| -12.14| -8.25| Cd > Fe > Cr > Zn > Cu > Pb |
| S5   | -9.72| -4.13| -6.73| -6.06| -12.14| -8.25| Cd > Fe > Cr > Zn > Cu > Pb |
| S6   | -9.62| -4.16| -6.77| -6.18| -12.14| -8.17| Cd > Fe > Cr > Zn > Cu > Pb |
| Result | | | | | | | Practically Unpolluted |

Table. 10 Results of Enrichment Factor

| S.No | S1 | S2 | S3 | S4 | S5 | S6 | EF -Quality | Result                      |
|------|----|----|----|----|----|----|-------------|-----------------------------|
| Fe   | 1  | 1  | 1  | 1  | 1  | 1  | -           | Pb>Zn>Cu>Cr>Cd              |
| Pb   | 36 | 36 | 45 | 49 | 49 | 45 | Extreme     | Pb>Zn>Cu>Cr>Cd              |
| Zn   | 12 | 12 | 12 | 13 | 14 | 12 | Significant | Pb>Zn>Cu>Cr>Cd              |
| Cu   | 10 | 9.5| 7.9| 8.4| 8.0| 7.7| Significant | Pb>Zn>Cu>Cr>Cd              |
| Cd   | 0.23| 0.24| 0.21| 0.22| 0.23| 0.21| Minimal     | Pb>Zn>Cu>Cr>Cd              |
| Cr   | 2.5| 2.77| 2.77| 2.79| 2.77| Moderate| Minimal     | Pb>Zn>Cu>Cr>Cd              |

Table. 11 Results of Contamination Factor

| S.No | S1    | S2    | S3    | S4    | S5    | S6   | Classification |
|------|-------|-------|-------|-------|-------|------|----------------|
| Fe   | 0.002959| 0.002824| 0.002421| 0.00223| 0.002209| 0.002353| Low Concentration |
| Pb   | 0.08  | 0.08  | 0.09  | 0.09  | 0.09  | 0.09  | Low Concentration |
| Zn   | 0.14  | 0.13  | 0.11  | 0.11  | 0.11  | 0.11  | Low Concentration |
| Cu   | 0.03  | 0.03  | 0.02  | 0.03  | 0.03  | 0.03  | Low Concentration |
| Cd   | 0.000444| 0.000444| 0.000333| 0.000333| 0.000333| 0.000333| Low Concentration |
| Cr   | 0.004828| 0.004598| 0.004368| 0.004023| 0.004023| 0.004253| Low Concentration |
Table. 12 Physio chemical Characteristics of Ground Water Samples.

| S.No | Parameter | L = 200 m | L = 400m | L = 600m | L = 800m | L = 1000m | L = 1200m |
|------|-----------|-----------|----------|----------|----------|-----------|-----------|
| 1    | pH        | 6.85      | 7.05     | 7.27     | 7.25     | 7.19      | 7.08      |
| 2    | EC        | 1615.95   | 2386.65  | 2253.30  | 2702.70  | 1841.70   | 2058      |
| 3    | TDS       | 1134.00   | 1446.90  | 1930.95  | 2363.25  | 1614.90   | 1263      |
| 4    | Ca⁺       | 65.10     | 117.60   | 168.00   | 147.00   | 50.40     | 111       |
| 5    | Mg²⁺      | 33.60     | 114.45   | 98.70    | 117.60   | 64.05     | 74        |
| 6    | TH        | 304.50    | 774.90   | 832.65   | 861.00   | 394.80    | 588       |
| 7    | K⁺        | 31.50     | 30.45    | 72.45    | 12.60    | 18.90     | 584       |
| 8    | Cl⁻       | 127.05    | 290.85   | 469.35   | 127.05   | 240.00    | 669       |
| 9    | SO₄²⁻     | 95.55     | 118.65   | 90.30    | 154.35   | 99.75     | 177       |
| 10   | Na⁺       | 204.75    | 218.40   | 128.10   | 201.60   | 305.55    | 569       |
| 11   | NO₃⁻      | 0.33      | 1.28     | 1.01     | 0.72     | 0.55      | 0.51      |
| 12   | F         | 0.70      | 0.36     | 0.89     | 0.76     | 0.14      | 0.41      |

Parameter | Min | Max | Avg | Median | SD  | Kurtosis | Skewness | Variance |
----------|-----|-----|-----|--------|-----|----------|----------|----------|
| pH       | 6.85| 7.266| 7.11| 7.13   | 0.16| 0.48     | -0.97    | 0.02     |
| EC       | 1616| 2702.7| 2143.0| 2155 | 390 | -0.59    | 0.08     | 152116   |
| TDS      | 1134| 2336 | 1621.0| 1531 | 448 | -0.26    | 0.76     | 200645   |
| Ca⁺      | 50.40| 168  | 109.90| 114  | 45  | -1.38    | -0.17    | 2072     |
| Mg²⁺     | 33.60| 117.6| 83.83 | 87   | 32  | -0.80    | -0.56    | 1059     |
| TH       | 304.50| 861  | 625.98| 681  | 236 | -1.98    | -0.47    | 55672    |
| K⁺       | 12.60| 72.45| 35.70 | 31   | 22  | 0.65     | 1.00     | 474      |
| Cl⁻      | 127.05| 669.9| 329.70| 292  | 209 | -0.06    | 0.82     | 44031    |
| SO₄²⁻    | 90.30| 177.45| 122.68| 109  | 35  | -1.04    | 0.87     | 1265     |
| Na⁺      | 128.10| 569.1| 271.25| 211  | 156 | 3.49     | 1.78     | 24489    |
| NO₃⁻     | 0.33 | 1.281| 0.73  | 0.64  | 0.35| -0.56    | 0.68     | 0.12     |
| F        | 0.14 | 0.8925| 0.54 | 0.56  | 0.29| -1.44    | -0.24    | 0.08     |

Table. 13 Comparison of Spotted Water with Water Quality Standards

| Parameter | Average | BIS (10500) - 1992 | WHO 1997 |
|-----------|---------|---------------------|----------|
|           |         | Desirable Limit     | Maximum Limit |
| pH        | 7.11    | 6.5-8.5             | MR 7.0-8.5 |
| EC        | 2143.0  | -                   | - 750 |
| TDS       | 1621.0  | 500                 | 2000     |
| Ca⁺       | 109.90  | 75                  | 200      |
| Mg²⁺      | 83.83   | 30                  | 100      |
| TH        | 625.98  | 300                 | 600      |
| K⁺        | 35.70   | -                   | 100      |
Conclusion

1. The pH level of leachate reveals that the nature of leachate is stabilised one and age old.

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