Sci.Int.(Lahore),28(3),3101-3104,2016 ISSN 1013-5316;CODEN: SINTE 8

DETERMINATION OF PHTHALATES LEACHING IN OPEN DUMPING SITE IN SUBURBAN AREAS OF LAHORE (A CASE STUDY)

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ABSTRACT: *Mehmood Booti is an open dumping site in Lahore which contains municipal, industrial and agricultural waste of different types. The study determines the amount of Phthalates leached in open dumping site of Mehmood Booti, Lahore. The three sampling points, S1, S2 and S3 were selected at site. From each sampling point, samples of soil were taken at depths of 0-5, 5-10, 10-15, 15-20 and 20-25cm. These samples were analyzed for the amounts of Di-ethyl Phthalate (DEP) in µg/g. The analysis was carried out using High Performance Liquid Chromatography (HPLC). Results show that the average values of DEP at sampling points # 1, 2 and 3 were 2.55±2.1%, 1.64±0.3% and 1.16±0.1% µg/g respectively. The average value of DEP in all samples comes out to be 1.78±0.8% µg/g, which shows a comparable result to previous studies.*

Keywords: Di-ethyl Phthalates, Endocrine disrupter, Retention time, Plasticizer.

1 INTRODUCTION

With the passage of time, the interest on the study of the impacts of synthetic chemicals on humans, plant life and the environment has increased. The result of these studies indicates that man-made and some naturally occurring substances in the environment may affect the normal functioning of the endocrine system in body of the organism thus classified as endocrine disrupting chemicals.

One of the most common industrial chemicals is phthalates. They are not only used to increase the flexibility and durability of plastic products, they are also used as additives and solvents in paints, dyes and insect repellents[1][2][3]. Phthalate esters (PAEs) have been categorized as Endocrine Disrupter Chemicals (EDCs)[4].

Among all types of phthalate esters, di-2 ethylhexyl phthalate (DEHP) and di-n-butyl phthalate (DBP) are most frequently used for various purposes. DEP as a plasticizer is used in packaging films, lubricant in food items, various types of tubing used for medical purposes[5]. Soil is a natural basin for many persistent and long-lasting harmful substances, including phthalate esters[6].

Mehmood Booti, is a dumping site, located in the North of Bund Road in Lahore and owned by the City District Government Lahore (CDGL). Presently, the solid waste is being openly dumped and no measures are being taken to control the leachate produced. The composition of waste affects the chemistry of the leachate that is generated in dumping sites. In developing countries like

Pakistan, the municipal solid wastes at such dumping sites has a high content of vegetable and fruit residues, leaves, grass, straws, dust, ashes, plastic and rubber majorly[7]. Due to the presence of plastic articles in waste, phthalate esters and other plasticizers are leached.

The study determines the presence and amount of Phthalates leached in open and uncontrolled dumping site of Mehmood Booti, Lahore. For this purpose, mainly three sampling points were selected and soil samples were extracted at various depths to determine the difference in the concentration of Phthalates detected.

2 MATERIALS & METHODS

2.1 Chemicals

All chemicals used were of analytical reagent grade except for mobile phase which was HPLC grade. Acetonitrile was HPLC Grade, double distilled water was used for dilutions and Diethyl Phthalate was analytical reagent grade.

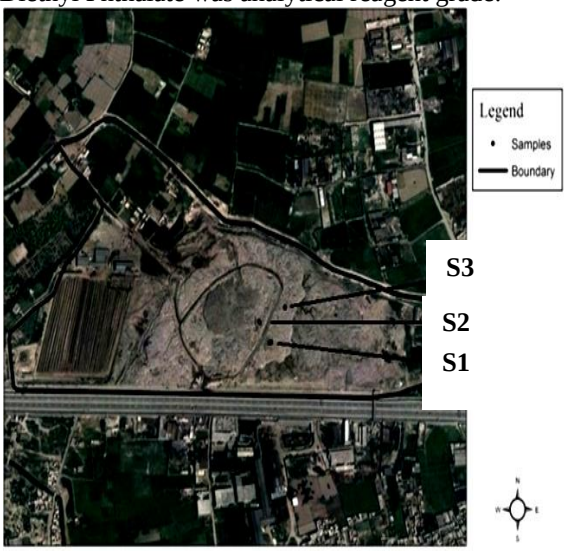


Figure 1 Location Plan of Sampling Points at Mehmood Booti

Sampling Plan & Collection

Soil samples were collected from the three (3 Nos.) sampling points from Mehmood Booti site. The Location of these samples is shown in Fig. 1.

Three random points for sample collection were selected at site depending upon the latitude and open leachate flow. The Global Positioning Device (GPS) was used to note down the co-ordinates from where the samples were collected. uPVC

3102 ISSN 1013-5316;CODEN: SINTE 8 Sci.Int.(Lahore),28(3),3101-3104,2016

pipes of 25cm length were hammered into the soil layers to collect samples from top soil to 25cm depth. Pipes were capped and stored for later use at -20ºC.

2.2 Extraction Method

MAE (Microwave Assisted Extraction) was used for the extraction of phthalates from soil samples. Microwaves can easily penetrate into the sample, heating the solvent trapped in pores evenly. Compared to Soxhlet and ultrasonic extraction methods. MAE is preferable, due to consumption of small amount of solvents, possibility of stirring of sample and about 20-30mins per batch of as many as 12 samples can be performed.

Acetonitrile is used as an extraction solvent for phthalates. It has better extraction efficiency over other solvents because of dipole moment and an ability to dissolve wide range of ionic and non-polar compounds. Also, it is further used as a mobile phase in HPLC.

2.3 High Performance Liquid Chromatography (HPLC)

HPLC technique was used to separate out, identify and quantify the components in a mixture**.** PerkinElmer Series 200 HPLC coupled with UV/VIS Detector transmitting at 254 nm and C-18 Column was used for analysis. Flow rate used was 1.0ml/min and the column was operated using a mixture (mobile phase) of 70% Acetonitrile and 30% Water. HPLC was used for both Qualitative and Quantitative analysis of Phthalates in the samples.

2.4 Validity of Method

The analytical parameters of the method including linearity, precision (inter-day and intra-day), and limits of detection were validated.

Linearity of the method was evaluated by plotting calibration curve in the range of 1 to 1000ppm with triplicate analysis. It was found to be linear over this range selected with acceptable correlation coefficient (r^2 = 1.00). Limit of Detection (LOD) and Limit of Quantitation were calculated using relationship between standard deviation of the response and the slope of the calibration curve. The LOD and LOQ were 1.40 and 4.24g/g respectively. Precision of standard for peak area and retention time were calculated. Table 1 represents the within-day and between-day repeatability in terms of Percentage Relative Standard Deviation (% RSD). RSD value within-day precision for retention times was 0.18% and 1.29% for peak areas. While, between-day RSD value for retention times was 0.33% and 3.44% for peak areas, showing that the method is reproducible

Table 1 Evaluation of Method

Within day RSD %		**Between-day RSD %**		**Slope**	**Intercept**	**r^2**	**LOD g/g**	**LOQ g/g**
t **min**	Peak Area µV.s	*t* min	Peak Area µV.s					
0.18	1.29	0.33	3.44	443.7	219.4	1.0	1.40	4.23

2.5 Robustness

The parameters that were used to check robustness included variation in temperature, rinse time and injection volumes. No significant change was seen for variations in temperature, rinse time and injection volumes. The method proved to be robust.

3 RESULTS AND DISCUSSION

3.1 Standard (Di-ethyl Phthalate)

Figure 2 shows the chromatogram of di-ethyl phthalate of concentration 1000ppm obtained after analysis on HPLC. Peak obtained at retention time of 6.36 min corresponds to the standard peak.

Table 2 shows the summary of the results of three sampling points obtained and analyzed for concentrations of DEP.

The results reveal that the concentration of DEP in µg/g decreases at each sampling point as we move from top soil to deeper layers of soil. This is because the plastics are dumped on the top soil, the leachate produced as a result of heat and weather changes has the highest concentration of DEP in top layers.

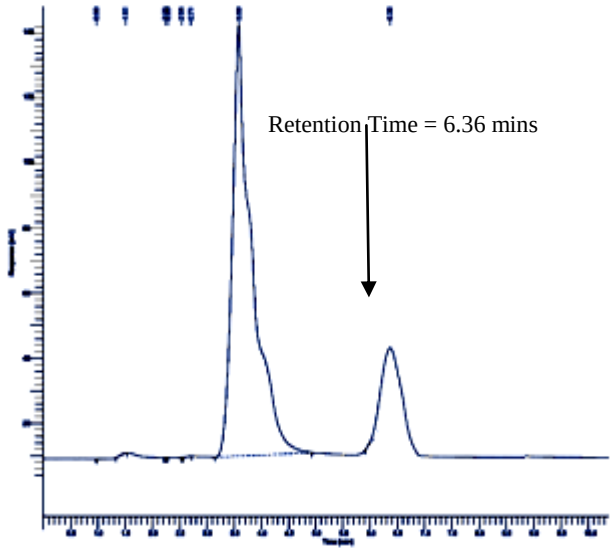


Figure 2 Chromatogram of Di-ethyl phthalate (DEP) of concentration 1000ppm at retention time of 6.36mins using Detection wavelength of 254nm, flow rate 1.0ml/min and a mixture (mobile phase) of 70% Acetonitrile and 30% Water.

Table 2: Concentrations (µg/g) of DEP in samples from three sampling points.

Sr.	Sample.	Concentration(µg/g)
Sampling Point 1		
1	S11	9.132 ± 6.3%
2	S12	1.804 ± 0.5%
3	S13	0.807 ± 0.7%
4	S14	0.689 ± 1.6%
5	S15	0.294 ± 1.7%
Sampling Point 2		
1	S21	3.863±0.3%
2	S22	1.913±0.2%
3	S23	1.428±0.1%
4	S24	0.709±0.2%
5	S25	0.291±0.5%
Sampling Point 3		
1	S31	2.157±0.1%
2	S32	1.117±0.1%
3	S33	1.006±0.1%
4	S34	0.934±0.1%
5	S35	0.586±0.3%

3.2 Sampling Point # 1

The bar graph shown in Figure 3 shows that as we move down from top soil to a depth of 25cm, the concentration of DEP in µg/g decreases. Sample 1 at a depth of 0-5cm, shows the concentration of 9.132±6.3% µg/g, which decreases to 1.804±0.5% µg/g at a depth of 5-10cm. This concentration further decreases to 0.807±0.7% µg/g in Sample 3, 0.689±1.6% µg/g of soil in Sample 4 and decreases to minimum in Sample 5, i.e. 0.294±1.7% µg/g. At sampling point # 1, the concentrations of DEP are in the range of 9.132±6.3% to 0.294±1.7% µg/g, with an average value of 2.54±2.1% µg/g. The trend depicted in the bar graph tells us that the leaching of phthalates decreases when we take samples at greater depths than at top soil. S1 represents a point on site which contains the leachate coming from a number of other locations due to gravity flow. Since the dumping site is uncontrolled, the proper system of leachate collection is absent at site and hence some points contain more concentration of phthalates than others.

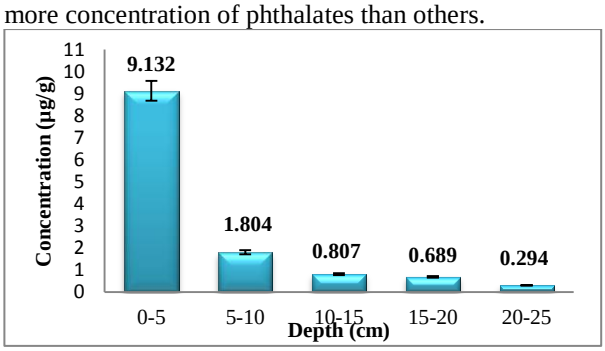


Figure 3: Bar graph showing a trend between depth (cm) of soil sample and Concentration of DEP (µg/g) in samples collected at Sampling Point # 1.

3.3 Sampling Point # 2

Similar trend (Figure 4) is seen at sampling point # 2 as at sampling point # 1. The concentration of DEP in samples decreases as we move from top soil to deeper soil samples. The concentration of DEP in $S2_1$, $S2_2$, $S2_3$, $S2_4$ and $S2_5$ is 3.863±0.3%, 1.913±0.2%, 1.428±0.1%, 0.709±0.2% and 0.291±0.5% µg/g respectively. This trend can be seen in Figure 4 where bar graph is clearly seen with decreasing DEP concentrations in samples. At sampling point # 2, DEP is in the range of 3.863±0.3% to 0.291±0.5% µg/g, with an average value of 1.64±0.3% µg/g. This point is a higher point compared to the S1, hence due to less gravity flow of phthalates from nearby points, the concentration of phthalates at all depths is less.

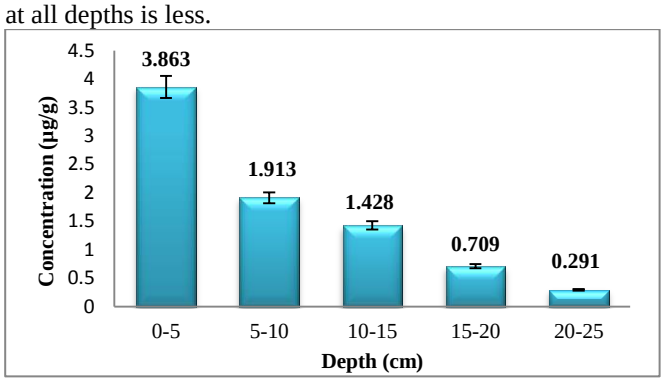


Figure 4: Bar graph showing a trend between depth (cm) of soil sample and Concentration of DEP (µg/g) in samples collected at Sampling Point # 2.

3.4 Sampling Point # 3

The bar graph shown in Figure 5 depicts that from depth of 0-25cm, the concentration of DEP in five samples gradually decreases. It is maximum in sample # 1, i.e. 2.157±0.1% µg/g, less in sample # 2 as compared to sample # 1, i.e. 1.117±0.1% µg/g. It further decreases to 1.006±0.1% µg/g, 0.934±0.1% µg/g and 0.586±0.3% µg/g in sample # 3, 4 and 5 respectively. The gradual decrease in the concentration of DEP from top soil to 25cm depth shows that leachate consisting of DEP decreases with the increase in soil depth. S3 represents a point where the quantities of plastics were less compared to other points. This may be because the scavengers pick up the plastics and other recyclable content for their use. At sampling point # 3, DEP is in the range of 2.157±0.1%-0.586±0.3%µg/g, with an average value of 1.16±0.1% µg/g.

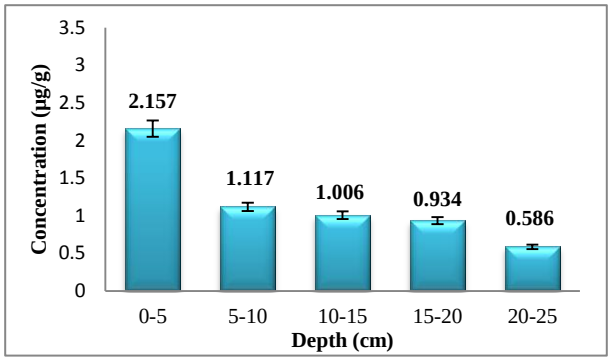
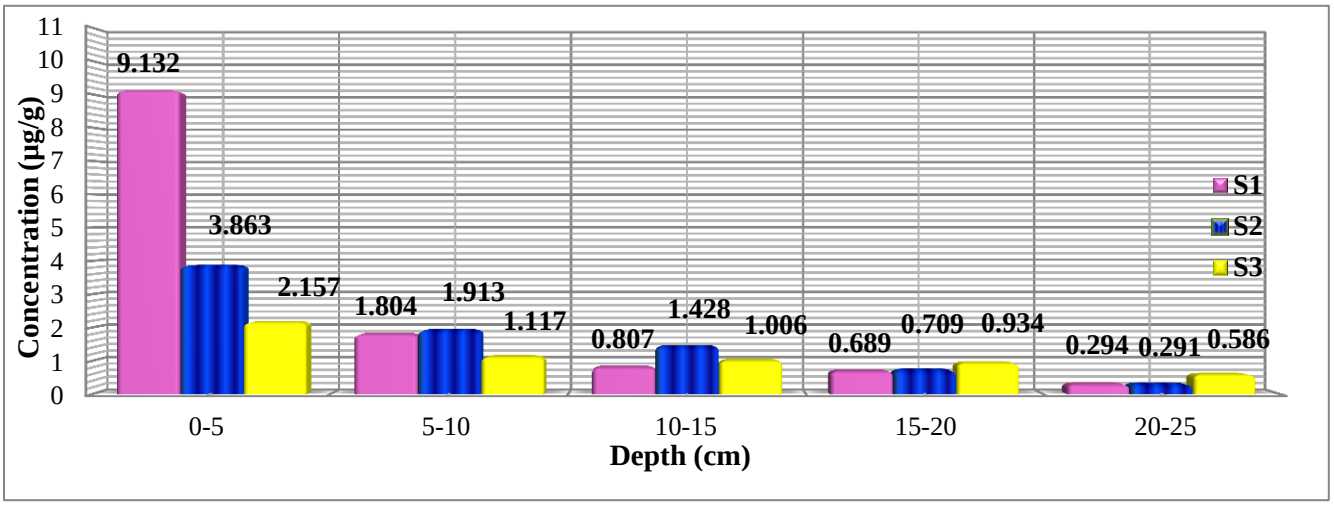


Figure 5: Bar graph showing a trend between depth (cm) of soil sample and Concentration of DEP (µg/g) in samples collected at Sampling Point # 3.

The overall trend of gradual decrease in the concentration of DEP in samples from 0-25cm soil depth can be shown in the combine bar graph, shown at Figure 6.

DEP was found in all samples. The average value for all samples comes out to be 1.78±0.8% µg/g. Indeed this is in the range of 0.794-19.504 µg/g with an average value of 2.975 µg/g, which shows comparable results to our study [8]. The results can be compared because Yellow River Delta in which the study was conducted is a highly urbanized and industrialized area of China like the Lahore city of Pakistan. Therefore, in both cases the origin of solid waste is municipal sewage and industrial material.

So far, no study has been conducted to determine the concentration of phthalates in the soil of Mehmood Booti Dumping site.



S1: Five samples at Sampling Point # 1, i.e. $S1_1$, $S1_2$, $S1_3$, $S1_4$ and $S1_5$ at depths 0-5cm, 5-10cm, 10-15cm, 15-20cm and 20-25cm respectively

S2: Five samples at Sampling Point # 2, i.e. $S2_1$, $S2_2$, $S2_3$, $S2_4$ and $S2_5$ at depths 0-5cm, 5-10cm, 10-15cm, 15-20cm and 20-25cm respectively

S3: Five samples at Sampling Point # 3, i.e. $S3_1$, $S3_2$, $S3_3$, $S3_4$ and $S3_5$ at depths 0-5cm, 5-10cm, 10-15cm, 15-20cm and 20-25cm respectively

Figure 6: Collective trend between Depth(cm) of soil sample and Concentration of DEP(µg/g) in samples collected at Sampling Point # 1, 2 and 3

4 CONCLUSION

Solid waste management is a chief challenge in Pakistan. The solid waste on Mehmood Booti is being dumped openly at present and no practice is carried out to control the leachate produce, therefore the waste generated as a result of human, industrial and domestic activities can lead to hazardous impacts on the environment. Valuable recycled materials are being dumped on site due to lack of a proper primary and secondary waste segregation as well as recycling system.

5 REFERENCES

[1] R. Shanker, C. Ramakrishma, and P. K. Seth, "Degradation of some phthalic acid esters in soil," *Environ. Pollut. Ser. A, Ecol. Biol.*, vol. 39, no. 1, pp. 1–7, 1985.

[2] W. Ling, G. JIANG, Y. CAI, H. E. Bin, Y. WANG, and D. SHEN, "Cloud point extraction coupled with HPLC-UV for the determination of phthalate esters in environmental water samples," *J. Environ. Sci.*, vol. 19, no. 7, pp. 874–878, 2007.

[3] P.-C. Huang, C.-J. Tien, Y.-M. Sun, C.-Y. Hsieh, and C.-C. Lee, "Occurrence of phthalates in sediment and biota: relationship to aquatic factors and the biota-sediment accumulation factor," *Chemosphere*, vol. 73, no. 4, pp. 539–544, 2008.

[4] R. A. Rudel, D. E. Camann, J. D. Spengler, L. R. Korn, and J. G. Brody, "Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust," *Environ. Sci. Technol.*, vol. 37, no. 20, pp. 4543–4553, 2003.

[5] U. S. D. of Health and H. Services, "Agency for toxic substances and disease registry," *Toxicol. Profile Asbestos. Updat. Agency Toxic Subst. Dis. Regist.*, 1999.

[6] M. Ahel, N. Mikac, B. Cosovic, E. Prohic, and V. Soukup, "The impact of contamination from a municipal solid waste landfill (Zagreb, Croatia) on underlying soil," *Water Sci. Technol.*, vol. 37, no. 8, pp. 203–210, 1998.

[7] S. Haydar, H. Haider, A. J. Bari, and A. Faragh, "Effect of Mehmood Booti dumping site in Lahore on ground water quality," *Pak. J. Engg. Appl. Sci*, vol. 10, pp. 51–56, 2012.

[8] Y. Hongjun, X. Wenjun, L. Qing, L. Jingtao, Y. Hongwen, and L. Zhaohua, "Distribution of phthalate esters in topsoil: a case study in the Yellow River Delta, China," *Environ. Monit. Assess.*, vol. 185, no. 10, pp. 8489–8500, 2013.