

INTERNATIONAL SOCIETY FOR SOIL MECHANICS AND GEOTECHNICAL ENGINEERING



This paper was downloaded from the Online Library of the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE). The library is available here:

<https://www.issmge.org/publications/online-library>

This is an open-access database that archives thousands of papers published under the Auspices of the ISSMGE and maintained by the Innovation and Development Committee of ISSMGE.

Infiltration of a phthalate acid ester in a Brazilian tropical soil

Infiltration d'un ester acide de phtalate dans un sol tropical brésilien

S.M.C.M. Carrara & D.M. Morita

Department of Hydraulic and Sanitary Engineering, University of São Paulo, Brazil

M.E.G. Boscov

Department of Structures and Foundations Engineering, University of São Paulo, Brazil

ABSTRACT

Phthalate esters are used in industrial production of lubricants, glues, insect repellents and plastics. Among the phthalate esters, di-2-ethylhexyl phthalate (DEHP) was chosen because it is one of the most difficult to biodegrade. The aim of this work was to study the infiltration of DEHP into a Brazilian tropical soil, as preliminary step for the investigation of a bio-remediation technique. An experiment was carried out in an infiltration reactor. The soil was compacted inside the reactor at the in-situ dry unit weight, and DEHP was applied to the upper surface of the specimen as an emulsion. Water and soil samples collected in the reactor and analyzed by gas chromatography showed that DEHP was retained in the upper layer of the soil. In the case of an accidental spillage of DEHP in a soil with characteristics similar to the studied saprolite, a great fraction will be retained in a superficial layer, suggesting that containment techniques may be advantageous to reduce environmental impact.

RÉSUMÉ

Phthalate esters est utilisé dans la production industrielle de lubrifiants, les colles, les insectifuges et les plastiques. Di-2-ethylhexyl phthalate (DEHP) a été choisi parce que c'est un des plus difficile à biodégrader. Le dessein de ce travail était d'étudier l'infiltration de DEHP dans un sol tropical brésilien, comme une étape préliminaire pour l'investigation d'une technique de bio-redressement. Une expérience a été exécuté dans un réacteur d'infiltration. DEHP a été appliqué à la surface supérieure du spécimen du sol comme une émulsion. Les échantillons d'eau et sol ont recueilli dans le réacteur et analysé par la chromatographie de gaz a montré que DEHP a été retenu dans la couche supérieure du sol. Dans le cas d'un déversement accidentel de DEHP dans un sol avec les caractéristiques similaires au saprolite étudié, une grande fraction sera retenue dans une couche superficielle, suggérant que ces techniques d'endiguement peuvent être avantageuses pour réduire l'impact écologique.

1 INTRODUCTION

Phthalate esters are organic compounds used in industrial production of lubricants, glues, insect repellents and plastics (Giam et al., 1984). Di-(2-ethylhexyl)phthalate (DEHP) is utilized as a plasticizer because of its stability, fluidity and low volatility, being one of the most frequently employed additives in the manufacture of flexible polyvinyl chloride (Staples et al., 1997). DEHP is a diester compound of o-phthalic acid ($C_{24}H_{38}O_4$), with molecular weight of 390.56 g and specific weight of 0.986 g/cm³ at 20°C (Verschueren, 1996). The United States Environmental Protection Agency has listed six phthalate esters as priority pollutants, including the DEHP, due to potential risks to the environment and human health.

The phthalate plasticizers have been reported to be endocrine disrupting chemical (EDC), which constitute a class of substances that cause adverse health effects in intact organisms (Alda and Barceló, 2000) and could affect endocrine functions, like reproduction. EDCs could interfere in hormones responsible for the maintenance of homeostasis and the development of regulation processes.

Significant amounts of DEHP are released annually into aquatic and terrestrial environments, as consequence of spilling or discharge of non-treated industrial wastewater. Considering manufacture, applications and wastewaters disposal, approximately 1.8% of the total yearly production of DEHP is released in the environment (Berndtsson, 1984 apud Huber, 1996). Other sources quantified this amount in approximately 100,000 ton per year (Klöpffer, 1994).

Among the existent phthalates, DEHP is one of the most difficult to biodegrade. Due to the high production and widespread use, and to the tendency of hydrophobic substances to

bio-accumulate in aquatic organisms and to become adsorbed to soil particles, DEHP concentrations are generally low in water, and moderately high in soils and biota (Russel and McDuffie, 1986).

In Brazil, chemical products are usually transported by truck, and may be sometimes released to the environment through traffic accidents. The environmental agency of the State of São Paulo (CETESB) has a list, which is constantly being extended, of 727 registered contaminated sites, among which are areas contaminated with phthalates. Considering that São Paulo is a densely populated and highly industrialized region, this number is probably much bigger.

The aim of this work was to study the infiltration of DEHP through a saprolitic soil derived from gneiss, representative of a group of residual soils that cover large extensions of Brazil, particularly the outskirts of the metropolitan region of São Paulo, as a preliminary step in the investigation of a bio-remediation technique.

2 EXPERIMENTAL METHODOLOGY

2.1 Soil characterization

The researched soil, a saprolitic soil from gneiss with wide occurrence in the metropolitan region of São Paulo, was collected in the campus of the University of São Paulo. The soil is composed of 41% predominantly fine sand, 35% silt and 24% clay, and presents pH of 4.9. The specific gravity of the solids, G_s , was measured as 2.7. The major mineral constituents are kaolinite, quartz and mica.

2.2 Experiments in a reactor

A DEHP emulsion was applied on the upper surface of a soil specimen in a cylindrical reactor made of acrylic, with diameter of 50 cm and height of 120 cm. The reactor had 5 points for the collection of pore water samples uniformly distributed along its height. Bottles were connected to each point to store the samples until the collected volume was sufficient for chemical analysis. The soil was compacted inside the reactor in 9 lifts of 10 cm thick, resulting in 0.9m of total height. The dry unit weight of the soil specimen in the reactor was 17.6 kN/m³, which corresponds to in-situ unit weight, and the water content was 20%, which was expected to be the most favorable situation for in-situ bio-remediation. The total weight of the specimen was 311 Kg, corresponding to a dry mass of 259 Kg. The soil was saturated by infiltration of water through the top surface during 2 months before DEHP application. The emulsion was prepared mixing 26 g of DEHP with 2 liters of water, resulting in a soil contaminated with 100 mg DEHP/Kg dry soil.

After the complete infiltration of the emulsion, 10 liters of water were weekly applied at the top surface to enhance DEHP migration through the specimen. Water samples were collected in the five collection points and DEHP concentration was determined by gas chromatography. After 5 months, soil samples were extracted from each point of collection, and DEHP content in the soil was also determined by gas chromatography.

2.3 Analytical Methods

Soil pH was measured electrochemically according to USEPA Method 9045. Quantification of DEHP was carried out by gas chromatography in a Hewlett Packard 6890 chromatographer. Soxhlet extraction method 3540C (USEPA, 1996) was the procedure used for the extraction of DEHP from the soil samples; this process ensures intimate contact of the sample matrix with the extraction solvent to inject in the chromatographer. Extraction of DEHP in water was carried out according to Khalil et al. (1999).

A Hewlett Packard HP-5 fused-silica capillary column (cross-linked 5% methyl-silicone) of 30 m x 0.32 mm with a phase thickness of 0.5 µm was used to separate the analytes.

3 RESULTS

Table 1 presents DEHP concentration in the soil pore water as a function of depth and time after the application of the DEHP emulsion on the upper surface of the soil specimen.

Table 1 – DEHP concentration in the soil pore water

Point of collection	Depth (cm)	Time (days)	pH	Water Temperature (°C)	Concentration of DEHP in water (µg/L)
1	16.6	23	6.3	26.4	nd
		70	6.4	26.0	nd
		133	6.8	26.0	nd
2	33.2	50	5.9	26.4	1.7
		120	7.2	26.0	2.8
		133	6.7	26.0	nd
3	49.8	38	4.8	28.8	1.3
		89	6.3	26.0	1.4
		133	7.1	26.0	15.1
4	66.4	70	3.8	26.4	nd
		133	4.3	26.0	*id

* indeterminated

Measured pH values between 6 and 7 may be explained by the effect of DEHP percolation, as they are slightly higher than the pH of the water applied on the upper surface of the soil specimen. The low concentrations of DEHP in the soil pore water, on the other hand, indicate that the pollutant was retained by the soil particles. Despite the continuous introduction of water,

DEHP presents low solubility in water; therefore, the low measured concentrations may also be related to the low mobility of the pollutant. Staples et al. (1997) present some values of DEHP solubility in water obtained by different researchers, the majority of which are lower than 0.4 mg/L.

At the point of collection 4, the measured concentration in water was 3615.1 mg/L that is an unacceptable value, therefore, it was considered indeterminate in Table 1. This unexpected high concentration was observed, probably due to contamination of the sample during the chemical analysis. Point 5 was obstructed or clogged, so that no samples could be collected.

Figure 1 presents the reactor used in the infiltration experiment. The aluminum foil paper cover was intended to avoid DEHP photolysis.



Figure 1 – Infiltration reactor.

Table 2 presents DEHP content in the soil samples as a function of depth after 5 months of DEHP application on the surface of the soil.

Table 2 – DEHP content in the soil samples

Depth (cm)	DEHP content in soil (mg/Kg)
0-2 (top)	3885.2
16.6	1.4
33.2	0.1
49.8	0.1
66.4	0.2
83.0	0.2

It can be observed that almost all DEHP applied to the soil was retained in the upper 2 cm of the soil specimen in the reactor. These results confirmed previous laboratory column and batch tests (Carrara et al., 2002), which showed high adsorption and low mobility of DEHP through the studied soil.

Spillages of DEHP do not tend to infiltrate deeply into the subsoil, unless the soil layer presents preferential flow paths e.g. features that are much more permeable than the soil mass. Gen-

erally, saprolitic soil layers tend to be coarser with depth. The expected retention of DEHP is important information for the selection of feasible remediation techniques.

4 CONCLUSIONS AND RECOMMENDATIONS

This research showed that DEHP was retained in the upper layer of the soil, which may be a good prospect in the case of an accidental spillage of DEHP over a soil with characteristics similar to those of the studied saprolite. The soil acts as a barrier for the infiltration of the product due to the chemical interactions between the clay and DEHP. Efficient containment around the spill may restrict the contaminated area and lessen the consequent environmental impact.

ACKNOWLEDGMENTS

The authors would like to thank FAPESP (Fundação de Apoio à Pesquisa do Estado de São Paulo), CTH (Centro Tecnológico de Hidráulica) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the financial support.

REFERENCES

- Alda, M. J. L. and Barceló, D. (2000). Determination of steroid sex hormones and related synthetic compounds considered as endocrine disruptors in water by liquid chromatography- diode array detection-mass spectrometry. *Journal of Chromatography A*, v. 892, 391-406.
- Berndtsson, S. (1984). as cited in Beratergremium für umweltrelevante Altstoffe (BUA) der Gesellschaft Deutscher Chemiker, *Di(2-ethylhexyl)phthalat*, BUA-Stoffbericht, 4, 1986 apud Huber, W.W., Grasl-Kraupp, B. & Schulte-Hermann, R. 1996. Hepatocarcinogenic potential of di(2-ethylhexyl)phthalate in rodents and its implications on human risk. *Critical Reviews in Toxicology*, v. 26, n. 4, 365-481.
- Carrara, S.M.C.M., Morita, D.M., and Boscov, M.E.G. (2002). Infiltration and adsorption of a phthalate plasticizer in a Brazilian tropical soil. *Environmental Geotechnics*, eds. L.G. Mello e M. Almeida, A.A. Balkema Publishers, Lisse (4ICEG - 4th International Congress on Environmental Geotechnics, Proceedings, v. 1, pp. 231-235, Rio de Janeiro).
- Giam, C. S., Atlas, E., Powers, M. A., and Leonard, J. E. (1984). Phthalic acid esters, p. 67-142. *In*: O. Hutzinger (ed.), *The handbook of environmental chemistry*. Springer, Berlin, Germany.
- Huber, W.W., Grasl-Kraupp, B. & Schulte-Hermann, R. (1996). Hepatocarcinogenic potential of di(2-ethylhexyl)phthalate in rodents and its implications on human risk. *Critical Reviews in Toxicology*, 26 (4): 365-481.
- Khalil, M. S., Kelada, N., Sawyer, B., Zens, D. R., Tata, P., Lue-Hing, C. (1999). Comparison of one-step acidic extraction versus two-step basic and acidic extraction procedures for semivolatiles analysis of wastewater. *Water Environment Research*, v. 71, n. 3, p. 348-354.
- Klöpffer, W. (1994). Environmental hazard, assessment of chemicals and products. II. Persistence and biodegradability of organic chemicals. *Environ. Sci. Pollut. Res.*, v. 1, 108-116.
- Russel, D. J. and McDuffie, B. (1986). Chemodynamic properties of phthalate esters: partitioning and soil migration. *Chemosphere*, v. 15, n. 8, 1003-1021.
- Staples, C. A., Peterson, D. R., Parkerton, T. F. and Adams, W. J. (1997). The environmental fate of phthalate esters: a literature review. *Chemosphere*, v. 35, 667-749.
- US Environmental Protection Agency (1996) *Soxhlet Extraction Method 3540C*. CD-ROM
- US Environmental Protection Agency (1996) *Phthalate esters by gas chromatography with electron capture detection (GC/ECD)*. Method 8061A, 1996. CD-ROM
- Verschuereen, K. (1996). *Handbook of environmental data on organic chemicals*. 3. ed. New York: Van Nostrand Reinhold. 2051 p.