CHAPTER ONE

INTRODUCTION

1. Introduction

1.1. Water Pollution and its effect

The presence of organic and non-organic waste materials in water is a matter of increasing concern to the water industry, environmentalist and the public.

It has been estimated that that river water can contain up to 2000 different organic substances over a wide concentration range and many of these survive processing in the water treatment works and occurs in potable water possible health implications [1].

Besides organic occurring in the water as a direct result of industrial activity, there are those, which occur indirectly from other sources i.e. haloforms, organometallic compounds and nitrosamine [2]. All these affect the population size and biological productivity of the waterway. Contamination of food takes place in the consumption of food produced from livestock consuming contaminated water. Residual contaminants in drinking water may also threaten human health.

1.2. Malaysia and water pollution

In Malaysia, industrialization has brought along a serious pollution problem. Industrial and domestic wastes, which have been discharged without much concern, have resulted in the contamination of the rivers.

According to the environmental quality report published in 1989 by the Department of Environment (DOE) of Malaysia, out of 86 rivers monitored, only 49 were classified as clean, the subsequent reports in 1991 and 1994 and 1997 showed that this number decreased dramatically.

The West Coast of Malaysia has highest number of rivers with pollution problems, since it is the most industrialized and populated region.

1.3. Study of Phthalate Esters (PEs)

Phthalate esters which are also known as phthalic acid esters are actually esters of 1, 2 – benzenedicarboxylic acid and 1, 3 – benzenedicarboxylic acid according to the IUPAC nomenclature. Two -COOR groups being attached to a benzene ring can also characterize Phthalates.

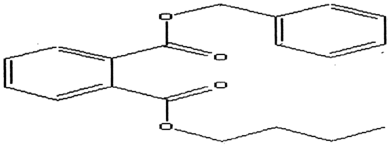
The alkyl group can be either the same or different. In this current study, only phthalates with the same alkyl group were studied since they are more commonly found in the environmental resources.

The structure of some of the common phthalate esters are given as follows:

Chemical Formula: $C_{19}H_{20}O_4$

Synonyms: BBP; n-Butyl Benzyl Phthalate; 1,2-Benzenedicarboxylic acid butyl phenyl methyl ester;

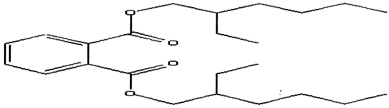
Chemical Structure:



Chemical formula: $C_{24}H_{38}O_4$

Synonyms: DEHP, bis (2-Ethylhexyl) phthalate;

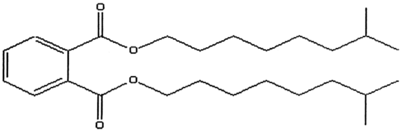
Chemical Structure:



Chemical Formula: $C_{26}H_{42}O_4$

Synonyms: 1,2-Benzenedicarboxylic acid diisononyl ester; bis (7-methyloctyl) phthalate; di-"isononyl" phthalate

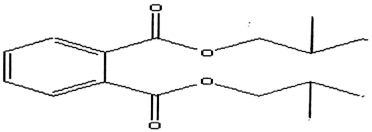
Chemical Structure:



Chemical Formula: $C_{16}H_{22}O_4$

Synonyms: DIBP; Dibutyl phthalate; n-Butyl phthalate; 1,2-Benzenedicarboxylic acid dibutyl ester;

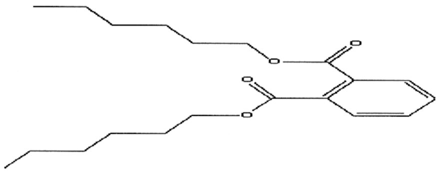
Chemical Structure:



Chemical Formula: $C_{20}H_{30}O_4$

Synonyms: 1,2-Benzenedicarboxylic acid, dihexyl ester; dihexyl ester phthalic acid; dihexyl phthalate

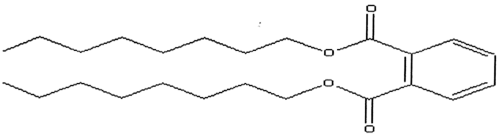
Chemical Structure:



Chemical Formula: $C_{24}H_{38}O_4$

Synonyms: DNOP; Dinopol NOP; n-Dioctyl phthalate; n-Octyl phthalate; bis (n-octyl) Phthalate, 1,2-Benzenedicarboxylic acid,

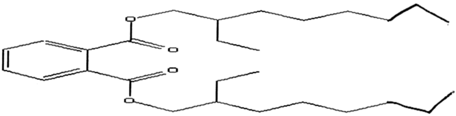
Chemical Structure:



Chemical formula: $C_{24}H_{38}O_4$

Synonyms: DOP; Dioctyl Phthalate; 1,2-Benzenedicarboxylic acid bis (2-ethylhexyl) ester;

Chemical Structure:



1.4. Introduction to Phthalate Esters

1.4.1. What are phthalate esters?

Phthalate esters are liquid plasticizers, similar in appearance to vegetable oils, which are added to a hard plastic called polyvinyl chloride (PVC or vinyl). The liquid phthalates act as a softener causing the plastic to become flexible.

For example, hard PVC with no plasticizer could be a pipe under a sink or the vinyl siding of a house. When plasticizers are added, a wide range of products can be created such as toys, wire and cable, flooring and shower curtains. Vinyl is actually the second most popular plastic in the world as a result of its durability, low cost and versatility.

1.4.2. How do plasticizers do their job?

PVC consists of long chain polymers with large (high molecular weight) strands of molecules. Plasticizers, such as phthalate esters, are liquids. The processing conditions -- involving heat and sometimes pressure -- force the polymers and the liquids together. In the new state, the liquid acts as an internal lubricant and allows the polymer chains to move relative to each other, i.e., provides flexibility. This material then can be molded or shaped into a variety of useful products. **[3]**

1.5. Health effects due to Phthalates

Plasticisers in general and phthalates in particular are currently the subject of considerable media, legislative and scientific debate. This is not new.

Concerns regarding plasticisers have been raised on a variety of topics at regular intervals ever since the early 1980's. These have included carcinogenicity, environmental effects, estrogenic activity and most recently exposure via toys. However, any fears have repeatedly been shown to be unfounded.

Despite the last forty years of research, work is still ongoing in the areas of carcinogenicity, reproductive and endocrine modulating effects. The current position is outlined below.

1.5.2. Carcinogenecity

The first indication that phthalates could cause an increased incidence of tumors in rats and mice was seen in 1980 in a two-year feeding study with DEHP carried out as part of the NTP/NCI Bioassay Programme in the United States.

At the same time it was established from mutagenicity studies that phthalates were not genotoxic. These findings triggered a large number of more detailed investigations on a variety of plasticisers, other chemicals and different animal species.

The aim of these studies, which are still ongoing, has been to discover the mechanism by which these non-genotoxic carcinogens cause tumors in rodents and to determine the relevance of these effects to humans. [4, 5]

1.5.3. Reproductive effects

Some phthalates, at high dose levels, have been shown to cause reproductive effects in rats and mice.

According to a review by the Commission of the European Communities [6] the most sensitive indicator of reproductive impairment by phthalates is testicular atrophy and the most sensitive species is the rat. They found the no effect level of DEHP for these effects to be 69-mg/kg body weights per day.

Recently it has been proposed [7] that the NOAEL for DEHP with regard to testicular effects in the rat should be as low as 3.7-mg/kg bw/day.

This is disputed because of shortcomings in the design of the study [8] and because its findings are at variance with many other more comprehensive studies both published and ongoing.

1.5.4. Endocrine modulation

As a consequence of their widespread usage phthalates have been one of the groups of chemicals, which have been tested for endocrine modulating effects using the recently developed in-vitro tests and the better established in-vivo ones.

Saying that the vast majority of phthalates have been shown to be inactive in in-vitro tests may summarize the in-vivo test data. Some, such as dibutyl phthalate (DBP) and butylbenzyl phthalate (BBP), appear to exhibit a weak positive result **[9,10]** indicating possible oestrogenicity. However, these findings are equivocal in that these phthalates have proved to be non-oestrogenic in other studies **[11]**.

1.6. Environmental effects

Phthalates are widely distributed in the environment however their levels are low because they are subject to relatively rapid photochemical and biological degradation.

Their levels are falling most likely due to improved effluent management.

Recent studies show that their impact on all environmental compartments is minor, however, due to their extremely low solubility in water, these studies are difficult to conduct and the results of earlier investigations must be treated with caution.

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1.6.2. Water solubility

Many values have been given for the solubility of DEHP in water ranging from 1 – 340 ppm **[12,13]**.

According to the latest Kow values measured by HPLC the water solubility for DEHP is 0.18-2.8 ppm.

It is now generally accepted that these lower values represent the true water solubility of phthalates **[14]** and that the higher ones reflect the ability of phthalates to form relatively stable and homogeneous dispersions in water under laboratory conditions.

Higher levels reported in the environment reflect the fact that the analytical extraction methods used do not differentiate between phthalates present in abraded PVC particles or adsorbed to organic matter suspended in water.

It is likely that phthalates in these forms will not be bioavailable.

1.6.3. Aquatic toxicity

It is well recognized that phthalates, due to their low water solubility, present special problems in aquatic toxicity testing.

This is especially true in the case of tests on Daphnia where it is very easy to try to force too much of the phthalate into solution and the observed effects are due to entrapment of the Daphnia at the surface rather than the toxicity of the test compound.

It is apparent that the conflicting data found in several chronic Daphnia studies are due to surface entrapment causing the Daphnia to become stressed and in many cases to die.

This conclusion is supported by the studies carried out on a number of phthalate esters in the presence of a non-toxic dispersant.

Under these conditions, at a concentration of 1 mg/liter, no surface entrapment occurs and the Daphnia are unaffected **[15]**.

In summary dihexyl to diundecyl phthalates, at concentrations up to their solubilities in water, produce no acute or chronic toxic effects in aquatic organisms.

1.6.4. Sediment toxicity

The toxicity of sediment-associated phthalates has been investigated in a comprehensive research project **[16]** carried out at the University of Wisconsin in conjunction with the US EPA.

In 10-day sediment toxicity tests with *Chironomous tentans* and *Hyalella azteca* no effects were observed for dihexyl, diethylhexyl, diisononyl, 711P and diisodecyl phthalate at the maximum concentration tested (3000 mg/kg dry weight).

These findings are in line with those of two other recent studies. A 28-day chronic sediment toxicity study for both DEHP and DIDP indicated no effects on the time to emergence or sex ratio of the midge (*Chironomus riparius)* at sediment concentrations up to 10,000-mg/kg dry weight **[17]**. In another study, no effects were observed on moorfrog (*Rana arvalis*) egg hatching or tadpole survival at the highest sediment concentrations tested i.e. 600-mg/kg dry weight for both DEHP and DIDP **[18]**. It should be noted that these concentrations at which no effects have been observed are orders of magnitude higher than those found in the environment.

1.6.5. Bioaccumulation

Reliable bioconcentration studies that maintain constant exposure concentrations over the course of the exposure period indicate a much lower, more consistent range of BCFs for phthalates, eg. around 120 for DEHP in the carp and 9.4 for BBP in bluegill sunfish **[19]**.

A comprehensive critical review of phthalate bioaccumulation literature is provided in the review paper of Staples et al.

1.6.6. Biodegradation

The water solubility of the higher molecular weight phthalates is much lower than the levels used in many laboratory biodegradation studies.

It follows that only a small part of the phthalate in the test system is available for biodegradation and consequently the test appears to indicate that these phthalates are not biodegradable.

The more recent work on DBP, DEHP and DINP **[20]** clearly demonstrates that these three phthalates are readily biodegradable. These studies were conducted using a modified Sturm test (OECD 1993, EEC 1992), which is specifically designed for testing substances of low water solubility.

1.7. Objectives

The current study, determination of phthalate esters in the Klang River water by application of gas chromatography (GC) with flame-ionization detector (FID) will be carried out.

GC-MSD (mass-selective detector) will be also used in the identification of phthalates compounds.

A BP-5 nonpolar capillary column will be used for the analysis of the river water.