THE SORPTION OF ORGANIC COMPOUND IN SOILS

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ABSTRACT

Nowadays, world is facing one of the most critical problem which is water scarcity. These become a factor to the usage of wastewater to the wastewater reuse application. Globally wastewater is used as irrigation water especially for crops in agriculture activities. The advantages of reuse of wastewater in agriculture such as conserves water, reduces pollution of rivers due to the wastewater treatment plan discharged and other surface water, conserves nutrients and reducing the need of artificial fertilizer, increases crop yields and provides a reliable water supply to farmers. Although the function of wastewater treatment plant has been well noted such as remove odor, bad tastes and settable solids inside the wastewater but there is still some organic compounds that be able to escape from the treatment process thus presence in the final effluent. One of the organic compounds that have been reported is polycyclic aromatic hydrocarbons (PAHs). The presence of these organic compounds in soil and water are mostly caused by the reuse of wastewater as irrigation water. Soil play important role in the distribution of PAHs to environment. Soil has properties to behave as a dual sorbent. Mineral matter of soil sorbs contaminant by adsorption while soil organic matter sorbs the contaminant by partitioning. In this study, soil samples were taken from top soil from agriculture soils and the contaminant was Benzo(a)pyrene. In sorption batch experiment, soil- water partition coefficient (K_d) and soil-water partition coefficient normalized to organic carbon (K_{oc}) determination were conducted in order to determine the sorption process of PAHs in these soils. The result shows the highest sorption coefficient (k_d) exhibit in Top soil 3 while Top soil 1 exhibit the lowest. Therefore Top soil 3 exhibit stronger bond with Benzo(a)pyrene. Organic matter plays a dominant role in partitioning process of Benzo(a)pyrene in all soil. As the organic content increases, the sorption coefficient also increases for all soil.

ABSTRAK

Kini, dunia sedang menghadapi salah satu masalah yang paling kritikal yang kekurangan air. Ini menjadi faktor kepada penggunaan air sisa ke dalam aplikasi penggunaan semula air sisa. Di peringkat global sisa digunakan sebagai air siraman untuk tanaman terutama dalam aktiviti pertanian. Kelebihan penggunaan semula air sisa dalam sektor pertanian seperti memelihara air, mengurangkan pencemaran sungai disebabkan oleh pelan rawatan air sisa yang dilepaskan dan air permukaan, memelihara nutrien dan mengurangkan keperluan baja tiruan, meningkatkan hasil tanaman dan menyediakan bekalan air yang boleh dipercayai untuk petani . Walaupun fungsi loji rawatan air telah juga berkata seperti menbuang bau, rasa lapuk dan pepejal boleh ditetapkan di dalam air sisa tetapi masih terdapat beberapa sebatian organik yang dapat lari daripada proses rawatan itu kehadiran di dalam efluen akhir. Salah satu bahan organik yang telah dilaporkan adalah hidrokarbon aromatik polisiklik (PAH). Kehadiran bahan organik dalam tanah dan air kebanyakannya disebabkan oleh penggunaan semula air sisa air pengairan. Tanah memainkan peranan penting dalam pengagihan PAH kepada alam sekitar. Tanah mempunyai ciri-ciri untuk bertindak sebagai pengerap dua. Bahan mineral tanah serab pencemar tanah oleh penjerapan manakala bahan organik tanah serab pencemar dengan pembahagian. Dalam kajian ini, sampel tanah yang diambil dari tanah atas daripada tanah pertanian dan bahan cemar adalah Benzo (a) pirena. Dalam eksperimen kumpulan penyerapan, pekali partition tanah-air (K_d) dan pekali partition tanah air normal kepada karbon organik (K_{oc}) penentuan telah dijalankan untuk menentukan proses penyerapan PAH di tanah ini. Hasilnya menunjukkan pekali penyerapan tertinggi (K_d) mempamerkan di tanah permukaan 3 manakala tanah permukaan 1 mempamerkan terendah. Oleh tanah permukaan 3 pameran ikatan yang lebih kuat dengan Benzo (a) pirena. Bahan organik memainkan peranan yang dominan dalam proses Benzo (a) pirena pembahagian dalam semua tanah. Sebagai meningkatkan kandungan organik, pekali penyerapan juga meningkat untuk semua tanah.

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ppm	–	Part per million
°C	-	Degree of Celcius
µm	-	Micrometer

LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing Method
FKASA	-	Fakulti Kejuruteraan Awam dan Sumber Alam
HPLC	-	High performance liquid chromatography
PAHs	-	Polycyclic aromatic hydrocarbons
NIFA	-	National Institute of Food and Agriculture
UNDESA	-	United Nations Department of Economic and Social Affairs
US-EPA	-	United Stated Environmental Protection Agency
USDA	-	United State Department of Agriculture
USGS	-	U.S. Geological Survey
UMP	-	University Malaysia Pahang

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, world is facing one of the most critical problem which is clean water. Clean water is very highly demanded for certain countries which strictly care to its citizen. The water supplied to our residential areas, industries and cities are from our surface water like lakes, rivers and seas. As our population and economic activities increases, water demand is also increasing at the same time. Besides for daily activities and industrial usage, water also is highly used in agriculture activities. These become a factor to the usage of wastewater to be reused and supplied as domestic water. For instance, in Singapore a treated wastewater has been used as a drinking water. Mostly wastewater is used to irrigation water for crops in agriculture activities. The usage of wastewater for crops irrigation has been practiced for long time ago. This is because the wastewater contain high amount of nitrogen, phosphorus and potassium. Besides wastewater reuse also can reduce the needs of artificial fertilizer in agriculture.

Although the function of wastewater treatment plant is to remove odor, bad tastes and settable solid inside the wastewater but there is still some organic compounds that be able to escape from the treatment plant thus presence in the final effluent of wastewater treatment plan. One of the organic compounds that have been reported is polycyclic aromatic hydrocarbons (PAHs). Min Yao et al., (2012) reported that dissolved and adsorbed PAHs were detected in the centralized wastewater treatment plant of a chemical industry zone in Zhejiang Province, China. Thao Pham (1997) reported there are about 0.26 tons of PAHs were discharged annually by Montreal Urban Community wastewater treatment plan to the St Lawrence River, Canada. Gou and Zhou (2005) reported that PAHs are organic pollutants that are widely distributed in the environment, very toxic, and very persistent. Mostly PAHs have different toxicity based on their chemical properties.

Human exposure to PAHs in many different ways such as through a contact with soil, water or air contaminated with these compounds. For long term effect, it may include cataracts, kidney and liver damage, and jaundice. Some PAHs such as naphthalene can cause in redness and inflammation on our skin. At the same time, breathing or drinking large amounts of naphthalene also can cause the breakdown of red blood cells. Most common PAHs that cause cancer in animals is Benzo(a)pyrene based on laboratory experiments.

1.2 Problem statement

The PAHs compounds are present in the final effluent for the vast majority of wastewater treatment plant. Luthy et al., (1994) reported that some PAHs are carcinogenic and more persistent in the environment. At the same time, Pashin and Bakhitova (1979) showed that PAHs act as mutagens and carcinogens with requirement of metabolic activation from interaction with microsomal enzymes present in many body cells. Carcinogens and mutagens have potential to increase the risk of cancer by altering cellular metabolism or damaging DNA in cells. As wastewater is thought as an alternative to fresh water to be used as irrigation water for crops thus a further assessment need to be conducted in order to ensure the safety of wastewater reuse in this application.

1.3 Objective of study

The objectives of this study are:-

i. To determine the soil-water partition coefficient (K_d) of the compounds in each soils.
ii. To determine the soil-water partition coefficient normalized to organic carbon (K_{oc}).
iii. To identify the factor that influences the sorption process of this compound in soils.

1.4 Scope of study

This study is focusing on the sorption of polycyclic aromatic hydrocarbons (PAHs) in three types of soils. The polycyclic aromatic hydrocarbons (PAHs) compound used was Benzo(a)pyrene for each soils.

1.5 Research outcomes

At the end of this study, the sorption coefficient of this organic compound in soils will be able to be obtained. It is important to estimate the relationship between organic matter and sorption coefficient of each soil. The equilibrium time attainment is required to estimate the maximum time of the reaction between Benzo(a)pyrene and soil particles. Organic matter plays a dominant role in partitioning process of Benzo(a)pyrene in all soil. As the organic content increases, the sorption coefficient also increases for all soil.

CHAPTER 2

LITERATURE REVIEW

2.1 Water scarcity

Water scarcity includes both water stress and water crisis. Water scarcity can be defined as the difficulty of obtaining sources of fresh water for use, because the depletion of resources meanwhile the water crisis is a condition where the available water which is unpolluted within the area is less than the area's demand. Frank (2004) stated an area to be characterized as "waste scarce" depends on the needs of human and environment, the fraction of the resource is made available and temporal and spatial scales used to define scarcity. According to United Nations Department of Economic and Social Affairs (UNDESA), around 1.6 billion people, or almost one quarter of the world's population facing this water scarcity. Frank (2004) reported there a large part of the 900 million people in rural areas that have an income below one- dollar per-day poverty line lack access to water for their livelihoods. Pruss et al., (2002) stated massive health impacts such as diarhoeal diseases affected to the lives of 2.18 million people three-quarters of whom are children younger than five years old are caused by lack of access to safe drinking water and sanitation, combined with poor personal hygiene. It has been reported from Yang et al., (2003) that the water use has been growing at more than twice the rate of population increase in the last decade. Water scarcity is both a natural and a human-made phenomenon.

2.2 Wastewater

Each community produces liquid wastes, solid wastes and air emission to environment. Metcalf and eddy (1991) mentioned wastewater is a liquid waste which is essentially the water supply of the community after it has been used in various applications. Wastewater may come from residences, institutions, commercial and industrial establishment. The wastewater must be treated properly before released to the environment because it is very harmful to human and environment. They also reported that untreated wastewater contains numerous pathogenic microorganisms that dwell in the human intestinal tract. Besides, Asano and Levine (1998) stated that wastewater contains useful materials, such as organic carbon and nutrients like nitrogen, potassium, zinc, boron, sulphur and phosphorus which required for agriculture activities. Figure 2.1 show schematic diagram of wastewater management infrastructure.

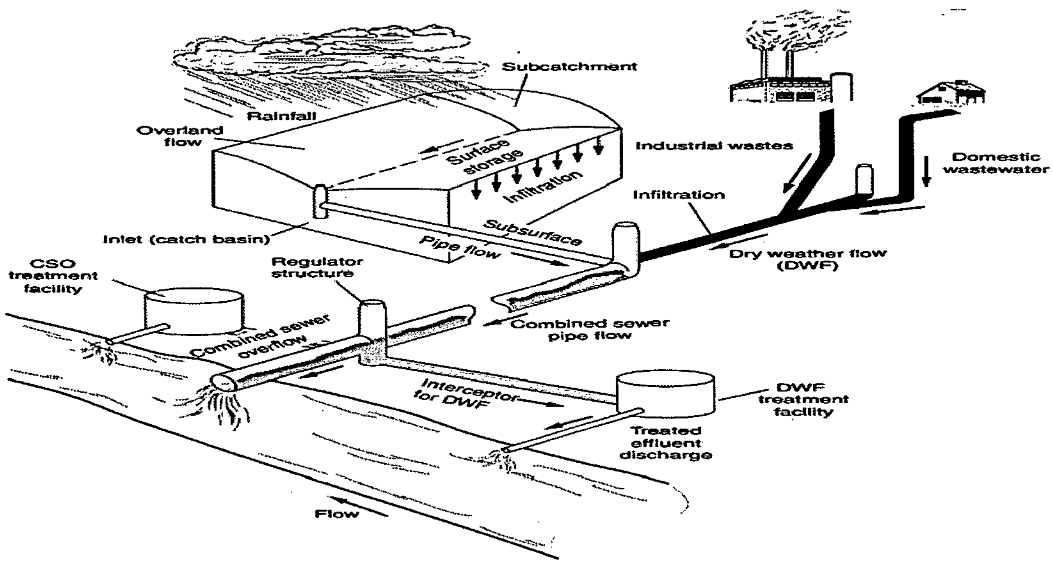


Figure 2.1: Schematic diagram of wastewater management infrastructure

Source: Metcalf and eddy (1991)

Wastewater often contains a variety of organic and inorganic compounds of anthropogenic and natural origin that potentially may be mutagenic or carcinogenic. The naturally occurring constituents in wastewater were present in the source water that was supplied to the user. From table 2.1, Eddy et al (1991) showed the physical characteristic of wastewater.

Table 2.1: Physical characteristic of wastewater

Characteristic	**Sources**
Physical properties:	
Color	Domestic and industrial wastes, natural decay of organic materials
Odor	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, soil erosion, inflow/infiltration
Temperature	Domestic and industrial wastes

Source: Eddy (1991)

Wastewater is generally divided into types which are black water and grey water. Black water refers to toilets waste and gray water refers to the remaining wastewater from sinks, showers, laundry and many more. These two types of wastewater are produced from residential sources. At the same time, non-residential wastewater is produced from restaurants, schools, hospitals, offices, industrials, institutional entities and many more.

2.2.1 Domestic Wastewater

Domestic wastewater means wastewater derived principally from dwellings, business buildings, institutions and etc. It also called as sanitary wastewater or sewage. It contains organic and inorganic matters which are in suspended, colloidal and dissolved form. The condition of the wastewater varies with the function of the water been supplied to the consumers. Moreover the presence of industrial wastes in public sewers had increasing the dangerous of the wastewater itself. According to Suthersan (1996), he stated that wastewater characteristic vary not only from the city to city but also season to season and even hour to hour within given city.

2.2.2 Industrial Wastewater

Industrial wastewater refers to process and non-process wastewater from manufacturing, commercial, mining, and civil cultural (forestry) facilities or activities. It also including the runoff and leachate from areas that receive pollutants associated with industrial or commercial storage, handling or processing and all other wastewater. There are some characteristic of industrial wastewater which is high temperature, suspended solids, oils, grease, acids and certain toxic chemicals including trace metals. Perhaps Suthersan (1996) also mentioned that one of most industrial wastes that must be mentioned is likehood of wide fluctuations in both flow and constituents of a waste.

2.3 Wastewater Reuse

Water scarcity associates with water pollution pose a critical challenge in our world. In urban areas, it is becoming difficult for authorities to manage water and wastewater. This phenomena leads to the strategies for wastewater reuse can improve urban management. The major factor of wastewater reuse is to reduce water scarcity in our world. Wastewater can be used in many sectors such as industry, urban uses, agriculture and environmental water enhancement.

According to National Institute of Food and Agriculture (NIFA), wastewater has been used as irrigation water to crops in agriculture sector. Asano and Levine (1998) stated that wastewater contains useful materials, such as organic carbon and nutrients like nitrogen, potassium, zinc, boron, sulphur and phosphorus. This usage of wastewater in agriculture reduced the use of artificial fertilizer and cost savings. There are a lot of advantages of wastewater reuse. Firstly, the reuse of treated wastewater can reduced water consumption and supports the water demand. Besides it also can save a lot of cost treatment of the wastewater. The treated wastewater can serves as a substitute water source which containing useful substances for some applications. As example, it can be used as toilet flushing and cooling water in residential and industrial sector. In fact, By reusing wastewater for many applications, more freshwater can be used for higher purposes such as drinking while contributing to further sustainable resource utilization. For instance, in Singapore a treated wastewater has been used as a drinking water.

2.3.1 Reused of wastewater in agriculture

The sector of agriculture is the biggest user of water all over the world. The water consumption for crop irrigation amounts more than 60% and sometime 90% of the world water demand. According to Ioannis et al., (2013), water shortage increasing at time when the increasing of world population food demand, urbanization, climate changes and poor quality water used.

Smit and Nasr (1992) estimated that at least 10% of the world population will consume agricultural products produced under wastewater reuse. Generally wastewater has been used as irrigation water to crops in agriculture. Joel (1996) mentioned that crop irrigation with wastewater has been practiced more than 100 years ago. There are a lot of benefits of wastewater reuse in agriculture sector. Liqa et al., (2007) stated that advantages of reuse of wastewater in agriculture such as conserves water, reduces pollution of rivers and other surface water, conserves nutrients and reducing the need of artificial fertilizer, increases crop yields and provides a reliable water supply to farmers. At the same time, she also mentioned disadvantages of wastewater reuse. There are health risks for the irrigators and communities who are in prolonged contact with untreated wastewater and consumers of the vegetables irrigated with wastewater, contamination of groundwater especially with nitrates, buildup of chemical pollutant in the soil, and creation of habitats for diseases vectors such as mosquitoes in peri-urban areas.

2.3.2 Organic contaminants in wastewater

Wastewater was produced from the usage of water of various activities of living things. The present of organic contaminants were detected in wastewater due to the usage of organic products and produced by excretion. Daughton (1999) reported there were increasing for potential adverse human and ecological health effect resulting from the production, usage, and disposal of numerous chemicals that offer enhancement in industry, agriculture, medical treatment, and even common household conveniences. Halling et al., (1998) reported that biogenic hormones, household chemicals, pharmaceuticals and other consumables are released directly to the environment after entering wastewater plant or domestic septic systems which are not designed to remove them from the effluent. Kolpin et al., (2002) also reported many organic contaminants include pharmaceuticals, hormones, detergents metabolites, fragrances, plasticizers and pesticides enter and leave WWTPs unfiltered or incompletely removed and present in the environment. Further study was conducted by U.S. Geological Survey (USGS) to assess whether these chemicals entering our Nation's streams from 139 stream. It shows that more than organic chemicals were detected in 80 percent of the streams sampled with low concentrations (less than 1 part per billion).

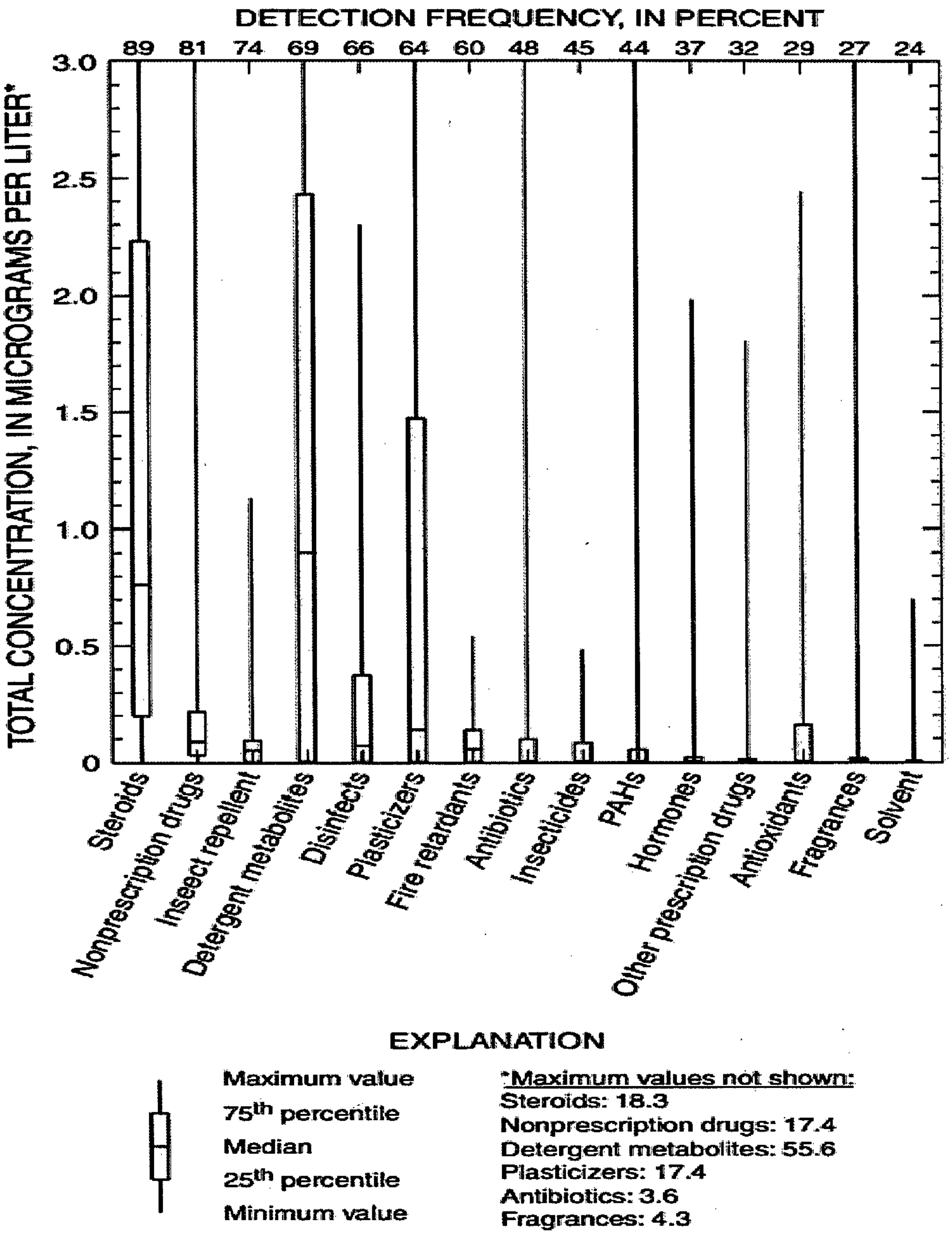


Figure 2.2: Organic chemicals detected based USGS study

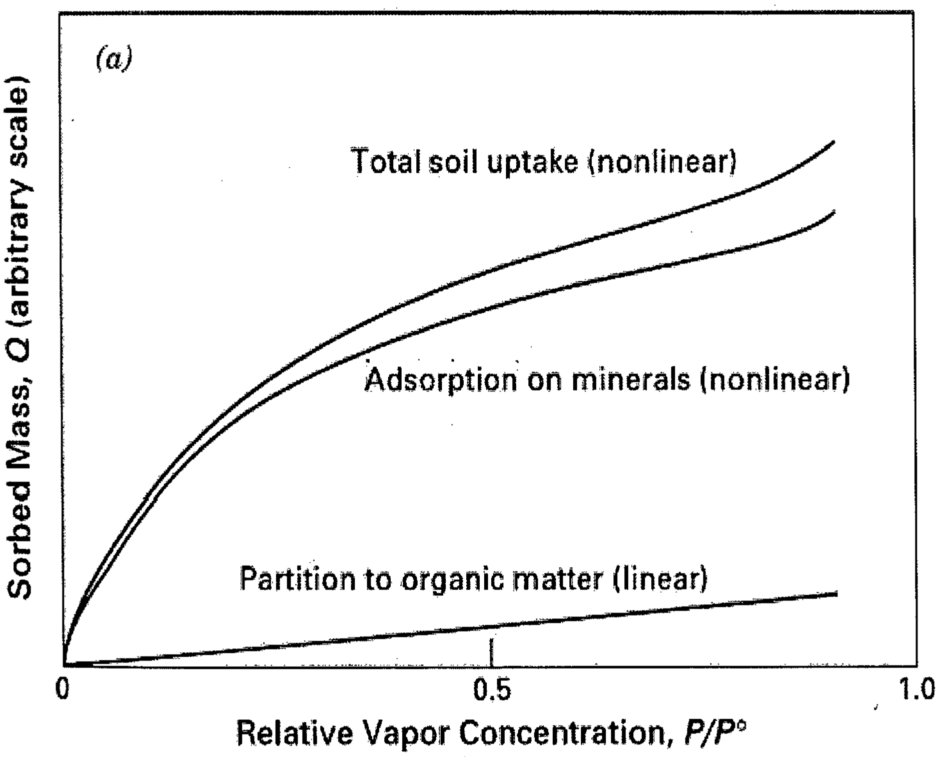
Source: USGS (2002)

2.4 Agriculture soil

Harlan and Hillel (1992) concluded that human use and management of soil and water resources have shaped the development, persistence, decline, and regeneration of human civilizations that are sustained by agriculture. Smith (1995) mentioned agriculture is a relatively recent human innovation that spread rapidly across the 10, 000 to 12, 000 years ago. Usually soil is referred as the fertile substrate and not all soils are suitable for growing crops. Singer et al., (2006) studied that the ideal agriculture soils are based on composition balanced of sand (0.05-2mm), silt (0.002-0.05mm), clay (less than 0.002mm), soil organic matter, air and water. There are a few types of soil mostly used in agriculture which are loam soils, sandy soils and clay soils. Loam soils usually known as medium textured soils which have balanced contributions of sand, silt and clay. This type of soils is very ideal for agriculture as they are easily cultivated and highly productive for crop growth. Meanwhile, characteristic of sandy soils are large pore spaces and can increase water drainage. Unexpectedly, sandy soils do not have many nutrients to be supplied to crops. For clay soils, it can increase water holding capacity and provide many sufficient nutrients required by crops.

2.4.1 Soil organic matter

Parikh and James (2012) summarized that soil organic matter comprises the partial or well-decomposed residues of organic biomass present in soil. Besides, they also mentioned the top soils are deep black colors and rich aromas which produced by soil organic matter. Based on United States Department of Agriculture (USDA), soil organic matter known as faction of the soil composed of anything that once lived which are includes decomposition of plants and animals, cells and tissues of soil organism, and substances from plant roots and soil microbes. It showed that organic matter in soil produced humus, a dark brown, porous, spongy material that has a pleasant and earthy smell. Usually, the amount of organic matter in soils is less than 5%. Generally, one of causes the distribution of organic compounds in soil is sorption in soil organic matter. In sorption process of organic compounds with soil, Chiou et al., (2012) have discovered that soil organic matter behaves primarily as a partition medium, rather than solid adsorbent. In further studies, they founded that the soil behaves as a dual sorbent based on the characteristic in the sorption of the organic compounds. They showed that mineral matter functions as a conventional adsorbent while soil organic matter as partition medium. Partitioning by soil organic matter can be determined by linear isotherm while adsorption by mineral matter for nonlinear isotherms. They also showed the contributions by adsorption on soil mineral matter and by partition to soil organic matter to up of an organic compound on figure.



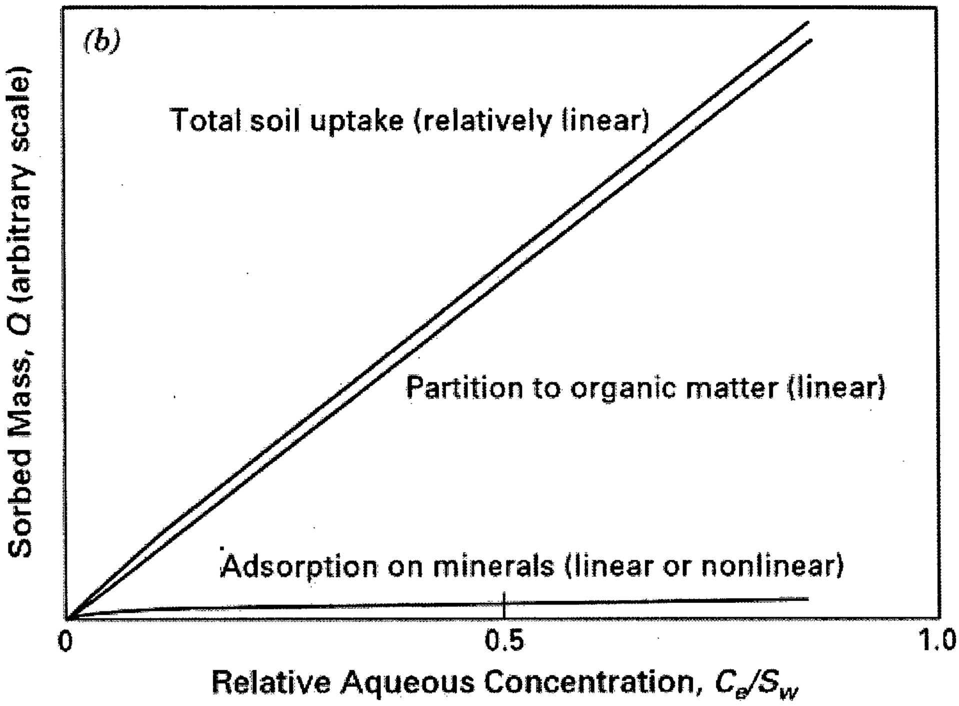


Figure 2.3: Contributions by adsorption on soil mineral matter and by partition to soil organic matter to up of an organic compound. (a) Uptake from vapor phase on dry soil (b) Uptake from water solution on wet soil.

Source: Chiou (2012)

2.5 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds composed of two or more benzene rings fused together. PAHs are products of incomplete combustion. PAHs are also known as polyarenes and polynuclear aromatic hydrocarbons. Generally, PAHs are generated and released to our environment by incomplete combustion of coal, oil and gas, garbage, or other organic substances like tobacco or charbroiled meat. Abbey et al., (2011) said PAHs compounds are forms and released into the environment through both natural and anthropogenic sources. The natural sources are including forest fires and volcanoes. Harvey (1997) stated that anthropogenic sources are:

- Combustion of fossil fuel, including motor vehicle emission and power generation
- Wood burning
- Municipal and industrial waste incineration
- Coal tar, coke, asphalt, crude oil, creosote, asphalt roads, roofing tar
- Discharges from industrial plants and wastewater treatment plants
- Hazardous waste sites, coal-gasification site , smoke houses, aluminum production plants
- Atmospheric contamination of leaf plants
- Cigarette smoke
- Charbroiled meat

In wastewater, Magdalini et al., (2005) mentioned that the present of PAHs are from industrial effluents and surface runoff. Anwar et al., (1998) mentioned that major source of PAHs as the recognized increasing discharged of municipal wastewater. Min Yao et al., (2012) reported that dissolved and adsorbed PAHs were detected in the centralized wastewater treatment plant of a chemical industry zone in Zhejiang Province, China. Thao Pham (1997) reported there are about 0.26 tons of PAHs were discharged annually by Montreal Urban Community wastewater treatment plan to the St Lawrence River, Canada. Moretti and Neufeld (1989) mentioned when activated sludge treated the wastewater, PAHs tend to accumulate in the sludge. This process had reducing a large portion of