

DETERMINATION OF GAS-PARTICLE PARTITIONING PARAMETERS AND INDOOR AIR CONCENTRATIONS OF SYNTHETIC MUSK COMPOUNDS

**A Thesis Submitted to
the Graduate School of Engineering and Sciences of
İzmir Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
MASTER OF SCIENCE
in Environmental Engineering**

**by
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**July 2013
İZMİR**

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ACKNOWLEDGMENTS

I would like to thank my advisor Prof. Dr. Aysun SOFUOĞLU for her helps throughout my thesis study. I would also thank to my co-advisor Assoc. Prof. Dr. Fikret İNAL and Assoc. Prof. Dr. Sait Cemil SOFUOĞLU for their support.

My special thanks go to my family : my parents, Zerrin and Cevdet ÖZCAN and my sister Gizem ÖZCAN for their endless love, encouragement, confidence and patience during my life. I would also thank my friends : especially Pınar KAVCAR ARCAN for her valuable support during my experimental study and also Burcu İLERİ, Gülçin ÜNAL TOSUN, Güneş DERMENCI, İrem ŞAHİN, Melis TOPRAK, Derya BAYTAK, Gamze KATIRCIOĞLU for their sincere friendship.

ABSTRACT

DETERMINATION OF GAS-PARTICLE PARTITIONING PARAMETERS AND INDOOR AIR CONCENTRATIONS OF SYNTHETIC MUSK COMPOUNDS

Gas-particle partitioning of compounds is the key process determining the fate of chemical in the environment. The partitioning process can be modeled depending upon dominancy of being adsorptive or absorptive partitioning and referred with partition coefficient (K_p $m^3.\mu g^{-1}$). K_p is related to liquid phase vapor pressure of a compound of interest. Due to difficulty related to model parameters, researchers have been developed a parameter called octanol air partition coefficient, K_{OA} which can be directly measured and used to estimate K_p .

Synthetic musk compounds (SMCs) are the one group of semi volatile organic compounds which are resistant to degradation, lipophilic and have moderate vapor pressures. They have been widely used in detergents, soaps, cosmetics, perfumes to give nice odorous effect for the product of interest. Most of their chemical properties values based on estimation methods. This study designed to measure octanol-air partition coefficients (K_{OA}) and supercooled liquid vapor pressures (P_L) by GC retention time method as a function of temperature to estimate gas-particle partitioning of SMCs. In addition ten indoor air gas and particulate phase samples were collected from a university cafeteria to determine experimental partition coefficient in the indoor air environment.

The log K_{OA} and log P_L values of synthetic musk compounds were ranged between 6.42 to 8.77 and 0.52 to -4.53, respectively at 25 0C . All of the compounds were detected in the gas phase and the concentrations ranged from 0.27 ng/m^3 to 106.8 ng/m^3 . In the particulate phase only DPMI, ADBI, ATII, MX and MK were detected in the range of 0.06 ng/m^3 to 210.5 ng/m^3 . Although the correlation between the gas-particle partitioning coefficient (K_p) and P_L was found as weak, K_{OA} was determined as a good descriptor for gas-particle partitioning process.

ÖZET

SENTETİK KOKU BİLEŞİKLERİNİN GAZ-PARTİKÜL DAĞILIM KATSAYILARININ VE İÇ HAVA KONSANTRASYONLARININ BELİRLENMESİ

Gaz-partikül dağılımı bileşiklerin çevrede bulunma durumlarını belirleyen önemli bir prosesidir. Dağılım prosesi adsorpsiyon yada absorpsiyonun baskınlığına bağlı olarak, dağılım katsayısı ($K_p \text{ m}^3 \cdot \mu\text{g}^{-1}$) aracılığı ile modellenebilmektedir. K_p bileşığın sıvı fazdaki buhar basıncı ile ilişkilidir. Model parametreleri ile alakalı zorluklardan dolayı, araştırmacılar direk ölçülebilen ve K_p 'nın tahmininde kullanılan oktanol-hava dağılım katsayısını K_{OA} geliştirmiştirlerdir.

Sentetik koku bileşikleri (SKB) yarı uçucu organik bileşikler grubundan olup bozulmaya karşı dirençli, lipofil ve orta seviyede buhar basıncına sahiptirler. Deterjanlarda, sabunlarda, kozmetikte, parfümlerde ürünlere hoş bir koku etkisi vermek için sıkılıkla kullanılmaktadır. Bu bileşiklerin birçok kimyasal özelliği tahmini metodlara dayandırılarak belirlenmiştir. Bu çalışma SKB'nin oktanol-hava dağılım katsayılarının (K_{OA}) ve aşırı soğutulmuş sıvı buhar basınçlarının (P_L) gaz kromatografik alikonma süresi yöntemi ile sıcaklığa bağlı olarak belirlenmesi ve gaz-partikül dağılımının tahmini için tasarlanmıştır. Ayrıca bir üniversite kantininden 10 adet gaz ve partikül faz örnekleri dağılım katsayının deneysel olarak belirlenebilmesi için toplanmıştır.

Sentetik koku bileşiklerinin $\log K_{OA}$ ve $\log P_L$ değerleri 25^0C sırasıyla 6.42 - 8.77 ve 0.52 - -4.53 arasında değişmektedir. Gaz fazında bütün bileşikler tespit edilmiş olup, konsantrasyonlar 0.27 ng/m^3 to 106.8 ng/m^3 arasında değişmektedir. Partikül fazında sadece DPMI, ADBI, ATII, MX and MK tespit edilmiş olup, konsantrasyonlar 0.06 ng/m^3 to 210.5 ng/m^3 aralığında değişmektedir. Gaz-partikül dağılım katsayısı ile P_L arasındaki korelasyon zayıf olduğu halde, K_{OA} gaz-partikül dağılım prosesi için iyi bir tanımlayıcı olarak belirlenmiştir.

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CHAPTER 1

INTRODUCTION

Synthetic musk compounds (SMCs) are used in various cosmetic products, detergents, air fresheners, perfumes and soaps (OSPAR 2000). Therefore, SMCs are defined in the category of personal care products by Environmental Protection Agency (EPA) of US.

SMCs are divided into three groups polycyclic musk compounds, nitromusk compounds and macrocyclic musk compounds. They are persistent organic pollutants that have adverse effects on human health and the environment. The production of the SMCs has been increased as a result of increasing demand. In the year 2000, the used amount of polycyclic musk compounds was 4000 tonnes (Salvito 2005). While musk xylene was used 67 tonnes, musk ketone was used 35 tonnes in 2000 (OSPAR 2000). Although no data obtained for the amount of polycyclic musk compounds and nitromusk compounds separately for Turkey, the used amount of the odorous cosmetic products was reported as 15146 tonnes in the Turkish Cosmetic and Cleaning Products Industrial Sector Report in 2007.

These compounds are persistent organic pollutants that have adverse effects on human health and the environment. As a result of high consumption, SMCs were detected in various environmental compartments such as water and wastewater (Yang and Metcalfe 2006, Peck and Hornbuckle 2004), sewage sludge and sediment (Chen et al., 2007, Simonich et al., 2002), biota (Nakata 2005, Yamagishi et al., 1981), human body and milk (Hutter et al., 2010, Lignell et al., 2008), ambient and indoor air (Kallenborn et al., 1999, Sofuoğlu et al., 2010). The fate, transport and transformation of the SMCs are important among these environments in order to indicate the possible fate and related effects.

SMCs are lipophilic and semivolatile organic compounds (SVOCs). The term lipophilic is defined by octanol-water partition coefficient (K_{ow}) values between 4.3 to 6 that also refers, the substances have low solubilities in water. The lipophilic character causes accumulation in fatty tissues and organic matter. Especially, macrocyclic musk compounds have high bioaccumulation potential because of their high K_{ow} values and

biodegradation of polycyclic musk compounds and nitro musks happen slowly in the environment (OSPAR 2000). As a consequence, lower biodegradation rates increase the background levels of chemicals and their presence in various environmental compartments varies as a result the exposure to these chemical varies as well. Inhalation would be an importatnt pathway in indoors for these chemicals due to mainly use of these chemicals in indoors. It is known that SMCs have adverse effects on human health and aquatic life where they have been studied a lot. Musk ambrette was found as mutogenic and banned by European Union in 1995. Musk xylene was also reported as a possible carcinogen (Rimkus and Brunn 1997). Polycyclic musk compounds have disruptive effect on the hormons in the body. HHCB and AHTN were determined as a stimulator for the estrogen receptors (Seinen et al., 1999).

Although the concentrations and some properties of SMCs were determined in different environmental compartments, not much data available about gas and particle phase concentrations of SMCs in air which is the major patways of transport of these type of chemicals. Therefore, there is not enough study to explain the behaviour of the SMCs in the atmosphere. These compounds are mostly 90 % present in the gas phase but they are subject to partitioning in atmosphere. Partitioning of compounds in the related compartment determines the fate of these compounds and exposure pathways of people. Therefore it is important to determine the parameters related to partitioning. In this study, the gas-particle partitioning parameters, octanol-air partition coefficients (K_{OA}) and supercooled liquid vapor pressures of SMCs were determined as a function of temperature for the first time. The experimentally measured data were also used to determine the gas particle partitioning values of each SMCs.

CHAPTER 2

LITERATURE REVIEW

2.1. Production of Synthetic Musk Compounds (SMCs)

Natural musk is a flavor produced by the male musk deer's (*Moschus moschiferus* L.) gland. Musk deer lives in the region of South Asia, East Asia, Southeast Asia and the eastern parts of Russia. A male deer produces 25 gr musk annually. Killing the male deer is not only way to obtain the musk pods. Actually, musk can be obtained from a live deer. But in general, the worth of the musk directs the hunters to illegal hunting. Musk is a very expensive product derived from an animal, that its price is more than gold in 1990s in Europe. There are some other animals and plants also produce odors similar to musk. The Muskrat *Ondatra zibethica*, The African Civet *Civettictis civetta*, The Russian Desman *Desmana moschata*, Musk Oxen *Ovibos moschatus*, The Suni *Neotragus moschatus* are the examples of animals and The Musk Mallow *Hibiscus abelmoschus*, The Musk Rose *Rosa moschata*, The Musk Milfoil *Achillea erba-rotta* are the examples of plants that produce musk odor. Musk has been used for 5000 years while preparing medicine and as a scent. Arab doctors sold musk to Western medicine as a tonic for heart, mind and chronic headaches. Musk were also taken to the Middle East by Arabs and it was used in the mortar of some mosques in Iran. St. Jerome first introduced Europe with musk at 390 AD. Previously because of the high cost and rareness, afterwards the concern of the conservation of the musk deer species, natural musks were replaced with the synthetically produced musk compounds. Synthetic musk compounds (SMCs) have been generally used in cosmetics, soaps, detergents, air fresheners as fragrance and fixatives for other odors (Homes and TRAFFIC 1999).

2.2. Structures and Properties of SMCs

SMCs are divided into three groups: Nitromusk compounds, polycyclic musk compounds and macrocyclic musk compounds. The first group nitromusk compounds

were first produced in 1890 (Gebauer and Bouter 1997). Musk Ketone (MK), Musk Xylene (MX), Musk Ambrette (MA), Musk Moskene (MM), Musk Tibetene (MT) are the commonly used nitromusk compounds. These compounds are lipophilic ($\log K_{ow} \geq 4$) and resistant to environmental degradation. After the determination of mutagenicity of Musk ambrette in 1995, it was banned by the European Union. In addition, the use of musk xylene was not recommended due to being a possible carcinogen (Rimkus and Brunn 1997). Skin could absorb 240 μg MX in a day (Bronaugh et al., 1998).

Polycyclic musk compounds were produced in 1950s (Gebauer and Bouter 1997). The first produced synthetic musk compound was phantolide (Rebmann et al., 1997). Due to efficient odor properties and the low price of the polycyclic musk compounds, they are more preferred in detergents and other cleaning agents (Sommer 2004). Cashmeran (DPMI), Phantolide (AHDI), Traseolide (ATII), Tonalide (AHTN), Galaxolide (HHCB), Celestolide (ADBI) are the polycyclic musk compounds commonly used. It was reported that 1473 tonnes of HHCB was produced in Europe for industrial use in 1998 (GRUNDSCHOBER 2000). Polycyclic musks are semivolatile and hydrophobic organic compounds like nitromusks. They have disruptive effect on the hormones in the body. HHCB and AHTN stimulate the estrogen receptors (Seinen et al., 1999). In the study of Schreurs et al., (2005), the results showed that HHCB and AHTN not only effect estrogen receptors but also the androgen and progesterone receptors. The last group of the synthetic musks are macrocyclic musk compounds and they were synthesized in 1926 (Pilz 1997). The structure of the macrocyclic musk compounds are very similar to the natural musks (Homes and TRAFFIC 1999). Hence difficulties in the synthesis of the macrocyclic musk compounds make them less preferable rather than nitro and polycyclic musks. Civetone, Muscone, Ambrettolide are some examples of the macrocyclic musk compounds. In Table 2.1 structures and important parameters of the synthetic musk compounds were shown.

Table 2.1. Synthetic Musk Compounds and Selected Physical and Chemical Properties

CAS Name	Common Name	Molecular formula	Molecular weight	Normal Boiling Point (K)	Melting Point (K)	log K _{ow} ^a	Chemical Structure
1-(1,1-dimethylethyl)-3,4,5-trimethyl-2,6-dinitrobenzene	Musk Tibetene	C ₁₃ H ₁₈ N ₂ O ₄	266.3	664	404.27	-	
1-(1,1-dimethylethyl)-2-methoxy-4-methyl-3,5-dinitrobenzene	Musk Ambrette	C ₁₂ H ₁₆ N ₂ O ₅	268.2	642.3	404.17	4.44	
1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene	Musk Xylene	C ₁₂ H ₁₅ N ₃ O ₆	297.2	665.3	425.88	4.90	
2,3-dihydro-1,1,3,3,5-pentamethyl-4,6-dinitro-1H-Indene	Musk Moskene	C ₁₄ H ₁₈ N ₂ O ₄	278.3	624.1	420.3	-	

^aGeyer et al., (2000)

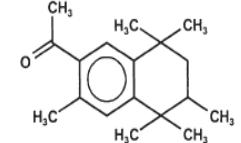
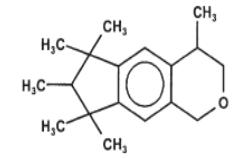
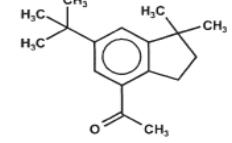
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Table 2.1. (cont.)

CAS Name	Common Name	Molecular formula	Molecular weight	Normal Boiling Point (K)	Melting Point (K)	log Kow ^a	Chemical Structure
1- 4-(1,1-dimethylethyl)-2,6-dimethyl-3,5-dinitrophenylethanone	Musk Ketone	C ₁₄ H ₁₈ N ₂ O ₅	294.3	642	432.51	4.20	
1,2,3,5,6,7-Hexahydro-1,1,2,3,3-pentamethyl-4H-inden-4-one	Cashmeran (DPMI)	C ₁₄ H ₂₂ O	206.3	559.1	343.77	4.50	
1-(2,3-Dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl)-ethanone	Phantolide (AHMI)	C ₁₇ H ₂₄ O	244.3	609.6	334.5	5.80	
1-[2,3-Dihydro-1,1,2,6-tetramethyl-3-(1-methyl-ethyl)-1H-inden-5-yl]-ethanone	Traseolide (ATII)	C ₁₈ H ₂₆ O	258.3	623	379.87	-	

(cont. on next page)

Table 2.1. (cont.)

CAS Name	Common Name	Molecular formula	Molecular weight	Normal Boiling Point (K)	Melting Point (K)	$\log K_{ow}^a$	Chemical Structure
1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone	Tonalide (AHTN)	$C_{18}H_{26}O$	258.3	629.8	379.87	5.80	
1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyrane	Galaxolide (HHCB)	$C_{18}H_{26}O$	258.3	599.3	375.64	5.90	
1-[6-(1,1-Dimethylethyl)-2,3-dihydro-1,1-dimethyl-1 <i>H</i> -inden-4-yl]-ethanone	Celestolide (ADBI)	$C_{17}H_{24}O$	244.3	582.1	369.07	5.40	

2.3. The Levels of the Synthetic Musk Compounds in Environmental Compartments

2.3.1. Water and Wastewater

Synthetic musk compounds exist in the wastewater as a result of the consumption of the cleaning agents, shampoos, detergents. The concentrations of the SMCs after the water treatment processes are important because the treated wastewater is again discharged to the water environments. Yang and Metcalfe (2006) determined the concentrations of SMCs in the wastewater of a domestic wastewater treatment plant in Canada. DPMI, ADBI, AHMI, ATII, HHCB, MX, AHTN and MK were found in the raw wastewater entered to the treatment plant. HHCB and AHTN were the dominant SMCs in the raw wastewater with the concentrations of 390 ng/L and 86 ng/L, respectively. MA, MM and MT were not detected in any raw wastewater samples. The measured final effluent concentrations were 3.9 ng/L, 2.9 ng/L, 2.7 ng/L, 7.3 ng/L, 173.1 ng/L, 6.4 ng/L, 41.5 ng/L, 8.4 ng/L for DPMI, ADBI, AHMI, ATII, HHCB, MX, AHTN and MK, respectively after treatment process. All of the SMCs in the raw wastewater were detected in the final effluent. The removal efficiencies were also investigated with using UV disinfection and without UV disinfection process. From the results, it was indicated that UV disinfection can not remove SMCs from the water.

Zeng et al., (2007) measured the polycyclic musk compound levels in the influent, primary and effluent waters from a municipal wastewater treatment plant in China. The concentrations were ranged from 0.38 $\mu\text{g/L}$ to 0.69 $\mu\text{g/L}$ for DPMI, 11.5 $\mu\text{g/L}$ to 146 $\mu\text{g/L}$ for HHCB and 0.89 $\mu\text{g/L}$ to 3.74 $\mu\text{g/L}$ for AHTN in influents. In this study it was pointed out that the main removal route of the synthetic musk compounds was the transfer of the compounds to the sludge and the removal efficiencies were 61-75% for DPMI, 86-97% for HHCB, 87-96 for AHTN. Chen et al., (2007) determined the polycyclic musks in a typical cosmetic plant's wastewater. The average DPMI, ADBI, AHMI, HHCB, AHTN concentrations in the influents were 24.94 $\mu\text{g/L}$, 6.54 $\mu\text{g/L}$, 4.70 $\mu\text{g/L}$, 549.68 $\mu\text{g/L}$, 64.60 $\mu\text{g/L}$, respectively. In the effluents DPMI, ADBI, HHCB and AHTN were detected. The removal efficiencies were 92.09%, 90.58%, 94.17%, 91.63% for DPMI, ADBI, HHCB and AHTN, respectively. Although the

removal efficiencies were high, the average concentrations were determined high in the range of 0.62 $\mu\text{g}/\text{L}$ to 32.06 $\mu\text{g}/\text{L}$ in the effluents.

The effluent waters from the wastewater treatment plants often carry the synthetic musk compounds to the surface waters. Peck and Hornbuckle (2004) determined the synthetic musk compound concentrations in Lake Michigan. The average water concentrations were the lowest 0.029 ng/L (ADBI) to highest 4.7 ng/L (HHCB), among the measured four polycyclic and two nitromusk compounds. DPMI was not detected in any samples. The sources of the SMCs in Lake Michigan were thought to be from atmospheric deposition, discharge from wastewater treatment plants, volatilization and outflow through the Straits of Mackinac. The results of the study showed that the major source of the synthetic musks in the water were the wastewater treatment plant discharges. Heberer et al., (1999) determined synthetic musk compounds in surface water by collecting samples from rivers, lakes and canals in Berlin. The high concentrations were found at the downstream of the sewage treatment plants. HHCB concentrations were ranged from 20 ng/L to 12500 ng/L while AHTN concentrations were ranged from 30 ng/L to 6800 ng/L. They came to a conclusion that polycyclic musk compounds indicated municipal sewage contamination in the surface water samples. Ramirez et al., (2011) detected DPMI, AHMI, HHCB, AHTN, MX and MK concentrations in the Ebro River in Spain. HHCB and DPMI concentrations were higher than other musk compounds. DPMI concentrations were ranged from 0.49 ng/L to 1.72 ng/L and HHCB concentrations were ranged from 1.40 ng/L to 26.2 ng/L. They indicated that musk ketone was found in river water samples although its use have been banned. They reported that musk ketone can still be found in the products despite banning.

Sea water is also a possible water environment that synthetic musks can be found. Xie et al., (2007) determined the air and sea concentrations of HHCB and AHTN in the North Sea and the Arctic. The concentrations were ranged from 12 pg/L to 2030 pg/L for HHCB. The maximum concentration of AHTN was 965 pg/L in the North sea. The high concentrations were especially found in the estuaries of the Elbe, the Weser and the Ems. In the Northeast Atlantic and the Arctic, HHCB and AHTN were not found because of the inavailability of discharge to this area.

As known drinking water sources are surface waters and groundwaters. Therefore the contamination of SMCs in surface and groundwaters can be transferred to the drinking water if the treatment for the removal is not sufficient. Wombacher and

Hornbuckle (2009) showed the background concentrations in the raw water and treatment efficiency for SMCs in a drinking water treatment plant. They investigated AHTN, HHCB, ATII, ADBI, AHMI, DPMI, MX and MK concentrations in the source of the drinking water and after the treatment in a Midwestern conventional drinking water plant with lime softening. All of the mentioned musk compounds except ADBI were detected in the river samples that supplied water to the treatment plant. The average concentrations were reported 180 ng/L, 0.8 ng/L, 7.3 ng/L, 0.15 ng/L, 2.8 ng/L, 0.06 ng/L, 0.07 ng/L for DPMI, AHMI, HHCB, MX, AHTN, MK, ATII, respectively. After the clearwell that is the last step of treatment plant, the concentrations of DPMI, AHMI, HHCB, AHTN were decreased to 9.9 ng/L, 0.06 ng/L, 2.2 ng/L, 0.51 ng/L, respectively. ADBI, MX, MK and ATII were not detected in the aqueous samples after the treatment. The sampling time was separated into two parts: cold weather and warm weather. The removal efficiencies for AHTN and HHCB were 79%, 70% in cold weather, respectively. In warm weather, while the removal efficiency of AHTN increased to 89%, the removal efficiency of HHCB decreased to 67%. They recommended that the studies for the improvement of the removal efficiencies of SMCs should be done in drinking water until completely treatment of SMCs. Another study about the concentrations of pharmaceuticals and endocrine disrupting chemicals in drinking water was done by Benotti et al., (2008) in the United States. Drinking water samples were collected from 19 drinking water treatment plant across to U.S. The maximum concentration of the galaxolide was detected 48 ng/L at the source of the drinking water. After the treatment the maximum concentration decreased to 33 ng/L and in the distribution systems galaxolide was not detected. Musk ketone, tonalide and traseolide were also not found in any samples.

The studies showed that SMCs has existed in many water environments and reached to the living things as a result of consumption of water. In Table 2.2, the detected concentrations of SMCs from the studies reported in literature in various water environments were shown.

Table 2.2. SMCs concentrations in various water environments

Sample Type	SMCs Concentrations (ng/L)										Reference	
	MT	MA	MX	MM	MK	DPMI	AHMI	ATII	AHTN	HHCB	ADBI	
Wastewater	-	-	-	-	-	-	-	-	580	1900	-	Bester (2004)
Wastewater (Enköping-Sweden)	-	-	-	-	-	-	4	-	90	336	7	Ricking et al., (2003)
Wastewater (Skene-Sweden)	-	-	-	-	-	-	2	-	42	218	3	Ricking et al., (2003)
Wastewater (Lancaster-Canada)	-	-	-	-	-	-	2	-	110	205	4	Ricking et al., (2003)
Wastewater (Raw influent)	-	-	13.6	-	14.5	8.5	4.8	18.9	85.9	390.2	5.8	Yang and Metcalfe (2006)
Wastewater (Effluent)	-	-	-	-	-	-	-	-	-	950-2050	100-140	Zeng et al., (2007)
Wastewater (Effluent)	-	-	-	-	-	1970	-	-	5410	32060	620	Chen et al., (2007)
Wastewater (Influent-Waterdown)	-	-	29.3	-	83.7	-	12	202	944	2411	32	Lee et al., (2003)
Wastewater (Effluent-Waterdown)	-	-	6.2	-	62.8	-	5	91	490	1170	15	Lee et al., (2003)

(cont. on next page)

Table 2.2. (cont.)

Sample Type	SMCs Concentrations (ng/L)											Reference
	MT	MA	MX	MM	MK	DPMI	AHMI	ATII	AHTN	HHCB	ADBI	
Wastewater (Influent)	-	-	376	-	569	-	-	-	10700	13700	-	Simonich et al., (2000)
Wastewater (Effluent)	-	-	5	-	99	-	-	-	1180	1170	-	Simonich et al., (2000)
Surface water (Wuhle, Marzahn)	<10	<10	<10	<10	390	-	-	-	6800	12500	520	Heberer et al., (1999)
Surface water (Erpe, Neuenhage)	<10	<10	180	170	70	-	-	-	90	70	60	Heberer et al., (1999)
River water	-	-	-	-	-	-	-	-	67	95	-	Bester et al., (1998)
River water	-	-	-	-	5	-	-	-	50	89	3	Winkler et al., (1998)
River water	-	-	-	-	-	-	-	-	46	141	-	Quednow and Püttmann (2008)
River water	-	-	n.d.-0.55	-	n.d.-0.80	0.49-1.72	n.d.-0.27	-	0.34-0.37	1.40-26.2	-	Ramirez et al., (2011)
Lake water	-	-	0.049	-	0.081	-	0.52	0.11	1.0	4.7	0.029	Peck and Hornbuckle (2004)
Lake water	-	-	-	-	-	-	70	70	530	1590	20	Fromme et al., (2001)
Sea water	-	-	-	-	-	-	-	-	-	0.012-2.03	<0.003-0.965	Xie et al., (2007)

n.d: not detected

2.3.2. Sewage Sludge and Sediment

SMCs reach wastewater treatment plants via wastewater as a result of consumption and accumulate in sewage sludge. The studies indicated that the removal of HHCB and AHTN by sorption on the sludge particles ranged from 50% to 90% that showed sludge was an important medium for the removal of the SMCs (Yang and Metcalfe 2006, Chen et al., 2007, Simonich et al., 2002, Bester 2004). The fate of synthetic musk compounds in the sludge should be also taken into consideration because when the untreated sludge were disposed to the sea, ocean, soil etc. and subject to volatilization to atmosphere from this environment after SMCs again released to the environmental compartments. Guo et al., (2010) investigated SMCs concentrations in the samples from 13 municipal wastewater treatment plant, 3 livestock wastewater treatment plant and 1 pharmaceutical wastewater treatment plant. The concentrations in the municipal wastewater plant samples were ranged from < limit of detection (LOD) to 0.250 mg/kg dry weight for ADBI, <LOD to 0.235 mg/kg dry weight for AHMI, 15.9 mg/kg dry weight to 82.1 mg/kg dry weight for HHCB, 4.48 mg/kg dry weight to 28.8 mg/kg dry weight for AHTN and <LOD to 1.32 mg/kg dry weight for MK. ADBI, AHMI and MK concentrations were under limit of detection in the industrial wastewater treatment plant sludge. The maximum detected HHCB concentration was 1.175 mg/kg dry weight in the livestock wastewater treatment plant sludge samples which was much more lower than the municipal wastewater treatment plant sludge. It was reported that HHCB and AHTN were the dominant polycyclic musk compounds in the sludge. Bester (2004) determined HHCB and AHTN concentrations in a sewage treatment plant sludges in Germany. The mean AHTN and HHCB concentrations were 1525 ng/g and 3068 ng/g, respectively. They reported that the optimization of the sludge/water ratio decreased the levels of HHCB and AHTN in a sewage treatment plant.

Chase et al., (2012) collected samples from surface water sediments in order to determine the levels of galaxolide, tonalide, celestolide, phantolide, traseolide, cashmeran, musk xylene and musk ketone in USA. They also took samples from the urban playa lake and suburban playa lake and their sediment where there was no wastewater inflow, to estimate the sources of the SMCs. In the sediment samples celestolide, phantolide, traseolide and musk xylene were detected in the range of not detected (n.d.) - 0.41 ng/g, n.d.- 1.91 ng/g, n.d.- 0.39 ng/g, n.d. – 0.70 ng/g,

respectively. Galaxolide and tonalide were not determined in any sediment samples from the urban playa lake. In the suburban playa lake only galaxolide (24.12 ng/g) and tonalide (10.21 ng/g) were detected in summer season. The main source of the SMCs were thought to be runoff and atmospheric deposition in these environments.

2.3.3. Biota

Awareness of synthetic musk compounds were started by the detection of SMCs in fish collected from the Tama River, Tokyo, in 1981 (Yamagishi et al., 1981). Musk ketone and musk xylene concentrations were detected 0.2 ppm and 0.05 ppm on wet weight basis, respectively. Then, Gatermann et al., (2002) investigated the bioaccumulation of synthetic musk compounds in freshwater fish and mussels taken from the pond of a municipal sewage treatment plant. Due to lipophilicity, the concentrations were determined on the lipid basis. MX levels were ranged from 18 ng/g lipid to 440 ng/g lipid in rudd, tench, crucian carp, eel and Zebra mussel samples. MK, HHCB and AHTN were also detected in all samples. SMCs were also determined in the marine mammals and sharks from Japanese coastal waters by Nakata (2005). In the blubbers of the finless porpoises HHCB concentrations were ranged from 13 to 149 ng/g on wet basis. The reason of the below detection limit concentrations for AHTN and nitromusk compound was reported that these compounds were used less or they have higher metabolic capacity in animals in Japan. In the livers of the sharks HHCB was also found between the range of 16 to 48 ng/g on wet basis.

2.3.4. Human Body

Hutter et al., (2010) investigated synthetic musk compound concentrations in the blood samples of women above fifty years old. According to the results, Galaxolide concentration was detected 6900 ng/L as the maximum concentration. The levels for the maximum concentrations of the synthetic musk compounds in the blood samples were ranging in the order of highest to lowest, Galaxolide, Tonalide, Musk Ketone, Musk Xylene, Cashmeran, Phantolide, Musk Ambrette, Musk Moskene, respectively. It was reported that the higher blood concentrations indicated higher consumption of the

lotions and cremes on the face and hands because above the fifty years old, people have much more dry skin which needs more care.

Another study was done by Lignell et al., (2008) about the concentrations of the musk compounds in the human milk in the United States. HHCB had the highest level among the other musk compounds in the milk samples. The concentration of HHCB was in the range of 5 to 917 ng/g. Musk xylene, musk ketone and AHTN were also detected. The concentrations were reported on a lipid weight basis. As synthetic musk compounds are lipophilic compounds, the higher concentrations in the lipid phases are expected.

2.3.5. Ambient and Indoor Air

The first study about the concentrations of the SMCs in ambient air was done by Kallenborn et al., (1999) in Norway. MX, MK, AHTN, HHCB and AHTN were detected 64 pg/m³, 45 pg/m³, 76 pg/m³, 223 pg/m³ and 15 pg/m³, respectively. After the study of Kallenborn et al., (1999), AHTN, HHCB, ATII, ADBI, AHMI, DPMI, MX and MK concentrations were measured by Peck and Hornbuckle (2004) in the air of Lake Michigan. The average AHTN and HHCB concentrations were detected 0.49 ng/m³ and 1.1 ng/m³ over the lake. While DPMI was not detected in any ambient air samples, MX concentrations were ranged between 0.014 ng/m³ to 0.046 ng/m³. Peck and Hornbuckle (2006) were also investigated the SMCs levels in urban and rural area of the Iowa and the Great Lakes. The median HHCB concentrations were ranged from 0.036 ng/m³ to 0.80 ng/m³. ATII, AHMI and MK concentrations were found below minimum reporting limit in all samples.

Synthetic musk compounds must reach the respiratory organ and interact with the odorous receptor system in order to perceive the odorous effect. Thus, inhalation is the most important pathway to exposure the SMCs with respect to dermal exposure and ingestion pathways. The first study about the concentrations of synthetic musk compounds in indoor air was done by Kallenborn et al., (1999).

Kallenborn and Gatermann (2004) were studied the levels of the synthetic musks in different indoor environments. Indoor air samples were collected from rest facilities, toilet and cafeteria in the Norwegian Institute for Air Research and the hair dresser in Downtown, Kjeller. While ATII, AHTN, HHCB were detected in all samples, MX and

MK were not detected in cafeteria. The highest HHCB concentration was found 44.3 ng/m³ in the hair dresser and in all indoor environments HHCB had the highest level. In the cafeteria the order of the musk levels from the highest to the lowest concentration was HHCB> AHTN> ATII.

The other study in order to investigate the concentrations in indoor air , Sofuoglu et al., (2010) measured synthetic musk compound concentrations in primary school classroom and women's sport center. Musk concentrations were measured in both gas and particulate phases. The average gas phase concentrations of HHCB were 267.3 ng/m³ and 144 ng/m³ in primary school classroom and women's sport center, respectively. MK average gas phase concentration 0.12 ng/m³, was the lowest concentration in the primary school classroom. In the study, it was reported that generally, musk compounds had a tendency to be in the gas phase rather than the particulate phase.

The studies about the concentrations in different indoor air environments were shown in Table 2.3.

2.4. Gas-Particle Partitioning of SVOCs in the Air

U.S. EPA Terminology Reference System defines the semivolatile organic compounds (SVOCs) as volatilize relatively slowly at 20 ⁰C (standart temperature) and 1 atm (standart pressure). SVOCs are the group of organic pollutants such as polycyclic aromatic hydrocarbons (PAH), organochlorine compounds (OCP), polychlorinated biphenyls (PCB) and synthetic musk compounds (SMC). These compounds have vapor pressures in an intermediate range and they are found in both gas phase and associated with particles in the atmosphere (Finlayson-Pitts and Pitts Jr 1999). If the vapor pressures of the SVOCs are < 10⁻⁶ Pa, they exist in the particle phase and if the vapor pressures are > 10⁻² Pa than they exist in the gas phase (Bidleman 1988). While explaining the fate, transport and transformation of the SVOCs, the partitioning between gas and particle phase plays an important role (Simcik et al., 1998). The determination of the total concentration for the SVOCs in the air depends on the partitioning between gas and particulate phase. The gas-particle partitioning process of the SVOCs is also important in both indoor and ambient air because of the human exposure to the compounds (Junge 1977, Pankow 1987, Pankow and Bidleman 1992). Since SVOCs

can deposit in the respiratory system, the effect of the deposition is strongly dependent on the gas-particle partitioning (Pankow 2001). Therefore, it is important to explain the gas-particle partitioning mechanism for both toxicology and atmospheric chemistry (Finlayson-Pitts and Pitts Jr 1999).

In the early studies about the gas-particle partitioning models, the assumption was mainly accepted that the partitioning mechanism of the semivolatile organic compounds exist only by physical adsorption (Pankow 1987, Yamasaki et al., 1982). Depending upon the composition of particulate matter in the atmosphere, either adsorption or absorption can be dominant mechanism in the partitioning. If the particulate matter in the atmosphere was mineral the sorption process will be based on physical adsorption and when the particulate matter content consists of some organic materials, the absorption process will be important in the partitioning (Pankow 1994). Partitioning processes are affected by the particle properties such as the particle size distribution, organic carbon content, TSP and the prevailing ambient temperature, etc. (Yeo et al., 2003). This partitioning process could be parameterized using equation (2.1) the gas/particle partition coefficient, K_p ($\text{m}^3/\mu\text{g}$) (Pankow and Bidleman 1992, Yamasaki et al., 1982, Pankow 1991).

$$K_p = \frac{F/TSP}{A} \quad (2.1)$$

where, F (ng/m^3) is the particulate phase concentration of the compound, TSP ($\mu\text{g}/\text{m}^3$) is the concentration of the total suspended particulate matter and A (ng/m^3) is the gas phase concentration of the compound. Hence equation (2.1) can not give any information about the partitioning process is whether absorption or adsorption or the combination of them by itself (Pankow 1994). If the partitioning mechanism is assumed to be adsorption, there is a correlation between the K_p and P_L according to the equation (2.2),

$$K_p = \frac{N_s a_{TSP} T e^{(Q_t - Q_p)/RT}}{2133 P_L} \quad (2.2)$$

where, N_s (sites/cm²) is the surface concentration of sorption sites, a_{TSP} (m²/g) is the specific surface area for the particulate matter, Q_l (kJ/mol) is the enthalpy of desorption from the surface, Q_v (kJ/mol) is the enthalpy of vaporization of the super- cooled liquid, R is the gas constant, T is the temperature (K), and P_L is the supercooled liquid vapor pressure (Pa) of the compound.

$$\log K_p = m \log P_L + b \quad (2.3)$$

According to equation (2.3) supercooled liquid vapor pressures (P_L) can be used to describe the gas-particle partitioning. If the plot of the $\log K_p$ versus $\log P_L$ with a slope of -1 that shows the relationship is linear, physical adsorption mechanism occurs. Sometimes deviations from the value of m , in the measurements can be observed. The deviations can be based on the temperature, concentrations of semivolatile organic compounds, relative humidity changes and non equilibrium. Under some circumstances, even at equilibrium, m will deviate from -1 due to the molecular interactions between the semivolatile organics and the solids (Finlayson-Pitts and Pitts Jr 1999). The absorption into the liquid organic layer surrounding the particle is as important as the adsorption on the particle, in the gas-particle partitioning process (Pankow 1994). If the absorption process is assumed as dominant, octanol-air partition coefficients (K_{OA}) can be used to determine the gas-particle partitioning coefficient (K_p) (Harner and Bidleman 1998). The relationship between K_p and K_{OA} was written in Equation (2.4)

$$K_p = K_{OA} f_{OM} MW_{OCT} \zeta_{OCT} / (\rho_{OCT} MW_{OM} \zeta_{OM} 10^{12}) \quad (2.4)$$

where, f_{OM} is the fraction of organic matter on TSP (total suspended particles), MW_{OCT} and MW_{OM} are the mean molecular weights of octanol and organic matter (g/mol), respectively, ρ_{OCT} is the density of octanol (0.820 kg/l), ζ_{OM} is the activity coefficient of the compound in the organic matter, ζ_{OCT} is the activity coefficient of the absorbing compound in octanol.

Table 2.3. Synthetic musk compounds in different indoor environments

INDOOR AIR		POLYCYCLIC MUSKS						NITROMUSKS	
Sample	Reference	HHCB	AHMI	ATII	AHTN	DPMI	ADBI	MX	MK
Laboratory	Kallenborn et al., (1999)	2.5	-	0.4	0.6	-	-	0.5	0.1
Laboratory	Kallenborn and Gatermann (2004)	5.6	-	0.3	1.9	-	-	0.3	0.1
Rest facilities	Kallenborn and Gatermann (2004)	19	-	0,8	5.8	-	-	0.6	0.2
Hair dresser	Kallenborn and Gatermann (2004)	44.3	-	5.2	13.4	-	-	1.0	0.3
Toilet	Kallenborn and Gatermann (2004)	18.9	-	0.8	6.2	-	-	0.4	0.1
Cafeteria	Kallenborn and Gatermann (2004)	35.3	-	4.8	11.6	-	-	n.d	n.d
Home	Regueiro et al., (2009)	143-1129	8.5	-	21-77	-	2.6	-	-
Rest Facility	Regueiro et al., (2009)	57	-	-	21	-	-	-	-
Classroom	Sofuoglu et al., (2010)	267.3	0.18	58.7	59.6	84.5	1.45	9.89	0.12
Women's sport center	Sofuoglu et al., (2010)	144	0.08	31	39.5	16.90	1.01	3.24	nd

n.d. not detected

When the activity coefficients of octanol and organic matter are assumed as equal and the ratio of the molecular weights of octanol and organic matter is equal to 1, equation (2.5), can be rewritten as,

$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91 \quad (2.5)$$

The gas-particle partitioning processes of the PCBs and PAHs were explained by using K_{OA} and P_L in ambient air (Simcik et al., 1998, He and Balasubramanian 2009, Cindoruk and Tasdemir 2007, Naumova et al., 2003). Although there are more studies about the gas-particle partitioning of the SVOCs in the ambient air, the studies in the indoor air are still insufficient. Naumova et al., (2003) investigated the gas-particle partitioning of PAHs in indoor and outdoor environments in order to show the effects of the outdoor air pollution on the indoor air pollution, using P_L as a predictor. Shoeib and Harner (2002) used K_{OA} and P_L as a predictor for the gas-particle partitioning of polybrominated diphenyl ethers (PBDEs) and perfluoroalkyl sulfomamides (PFASs) in indoor air. K_{OA} and P_L were found to be a good predictor for PBDEs. For PFASs because of the insufficient percentages of the particulate phase, the K_{OA} and P_L were not predicted the partitioning process sufficiently.

2.5. Octanol-Air Partition Coefficient (K_{OA})

A partition or distribution-coefficient is the ratio of concentrations of a compound in a mixture of two immiscible phases at equilibrium. These coefficients are the measure of the difference in solubility of the compound in these two phases. Normally one of the solvents chosen is water for the water soluble compounds while the second is hydrophobic such as octanol for organic compounds. From similarity, the developed octanol-air partition coefficient (K_{OA}) refers the ratio of the solute concentration in n-octanol to that in air at equilibrium present between air and octanol system. It is a key descriptor of the absorptive partitioning of SVOCs between atmosphere and organic phases found in soil, in vegetation, indoor carpet and on aerosols(Bidleman 1988, Hippelein and McLachlan 1998, Kömp and McLachlan 1997, Finizio et al., 1997, Won et al., 2000). The application of this parameter is based on the assumption that the interaction between the SVOCs and n-octanol, because octanol is

the surrogate compound for the organic fraction. K_{OA} is a useful parameter which is used to describe the interaction between the chemical and environmental organic phases that is assumed to be similar with the interaction between the chemical and n-octanol (Finlayson-Pitts and Pitts Jr 1999). The partitioning between the octanol and air phases can be expressed by equation (2.6),

$$K_{OA} = \exp(\Delta G_{OA}/RT) \quad (2.6)$$

where K_{OA} is the octanol-air partition coefficient, ΔG_{OA} (J/mol) is the Gibbs free energy of the partitioning from octanol to air, R (J/mol/K) is the ideal gas constant, and T (K) is the absolute temperature. Since the Gibbs free energy also depends on temperature, the temperature dependence of the octanol-air partition coefficient becomes more important. The temperature dependent values of K_{OA} used for the investigation of the partitioning process between air and organic phases.

2.6. Supercooled Liquid Vapor Pressure (P_L)

Supercooled liquid is a hypothetical liquid that does not crystallize when cooled below its melting point and the molecules move freely as at the liquid state. In the phase transfer processes the pure liquid compound is commonly used as the reference state. The supercooled liquid state is important because related to the changes in the chemical potential of the solid compounds at standard conditions, and the vapor pressure of the supercooled liquid corresponds to the reference state fugacity (Schwarzenbach et al., 2002).

At the equilibrium state, the pressure of the vapor of a compound with its pure condensed phase is described as the vapor pressure (P^0) of the compound that is solid or liquid (Schwarzenbach et al., 2002). It is important to know the vapor pressure of a compound due to the dependency of the partitioning between the environmental compartments. The partitioning of a compound in the atmosphere between gaseous and particulate phases is mainly determined by the vapor pressure. Vapor pressure is defined by many equations from Clasius-Clapeyron to Wagner which all of them relate temperature with vapor pressure. Clasius-Clapeyron equation is the basic equation used to explain the vapor pressure-temperature.

2.6.1. Thermodynamic Background

2.6.1.1. Clasius-Clapeyron Equation

The chemical potential is defined as the change in G(Gibbs function) with the addition of the substances added to the system.(i.e. pressure temperature)

$$\mu_J = \left(\frac{\partial G}{\partial n_J} \right)_{p,T,n} \quad (2.7)$$

where μ is chemical potential , n' is the other components other than J . Figure 2.1 is a phase diagram of a pure organic chemical where the pressure and temperature at the indicated phase regions are thermodynamically stable. The changes in the vapor pressures by temperature at the condensed phases were shown between the phase boundaries liquid-vapor and solid-vapor. At equilibrium the chemical potential of a compound is equal between the phases.

$$\mu_\gamma(p,T) = \mu_\theta(p,T) \quad (2.8)$$

where γ and θ are the phases in equilibrium. If the chemical potential of the phases are equal , the changes must be equal at equilibrium, therefore,

$$d\mu_\gamma = d\mu_\theta \quad (2.9)$$

$$d\mu_\gamma = -S_\gamma dT + V_\gamma dP \quad (2.10)$$

$$d\mu_\theta = -S_\theta dT + V_\theta dP \quad (2.11)$$

where S_γ and S_θ are molar entropies, and V_γ and V_θ are the molar volumes at the phases γ and θ . Then ,

$$\frac{dP}{dT} = \frac{\Delta S_{\gamma\theta}}{\Delta V_{\gamma\theta}} \quad (2.12)$$

Also at equilibrium,

$$\Delta G_{\gamma\theta} = \mu_{\gamma} - \mu_{\theta} \quad (2.13)$$

$$\Delta S_{\gamma\theta} = \frac{\Delta H_{\gamma\theta}}{T} \quad (2.14)$$

The equation (2.15) rearranges into the Clapeyron Equation :

$$\frac{dP}{dT} = \frac{\Delta H_{\gamma\theta}}{\Delta V_{\gamma\theta} T} \quad (2.15)$$

At the liquid-vapor boundary molar volume of the gas is much greater than the molar volume of the liquid so we can assume $\Delta V_{\text{vap}} \approx V(g)$ and with the assumption of ideal gas, $V(g) = RT/P$, now we can write,

$$\frac{d \ln P}{dT} = - \frac{\Delta H_{\text{vap}}}{RT^2} \quad (2.16)$$

Equation (2.16) is known as Clasius-Clapeyron Equation that commonly used in vapor pressure models.

2.6.1.2. Cox Equation

If the state of the compound does not change, as an example liquid to solid, in a narrow temperature range and any of the vapor pressure data is available for some temperatures, Clasius-Clapeyron equation can be used to calculate the vapor pressure of the compound at any chosen temperature. When the temperature range is enlarged,

Clasius-Clapeyron equation is insufficient to explain the temperature dependence of ΔH_{vap} . Cox (1936) rewrite the Clasius – Clapeyron equation as follows :

$$\ln P_R = A'(1 - \frac{1}{T_R}) \quad (2.17)$$

where P_R is defined as the ratio of the pressure and the normal boiling point pressure while T_R is the ratio of the temperature and the normal boiling point temperature. Here A' is assumed as a function of temperature by equation (2.18),

$$\ln A' = A + BT_R + CT_R^2 \quad (2.18)$$

A, B and C are the constants of the equation (2.18) and found from the non-linear regression analysis.

2.7. Methods for the Determination of K_{OA} and P_L

Octanol-air partition coefficients (K_{OA}) can be experimentally determined by direct and indirect methods. The generator column is a direct method that was developed by Harner and Mackay (1995), used for the determination of the K_{OA} . The octanol-air partition coefficients of chlorobenzenes, PCBs and DDT. Afterwards this method was used to measure K_{OA} of the various semivolatile organic compounds such as organochlorine pesticides and polybrominated diphenyl ethers (Shoeib and Harner 2002, Harner and Shoeib 2002). Purified air or nitrogen were used to saturate octanol with a defined flow rate. The octanol saturated gas stream was passed through a coil to exchange the temperature of the gas from the initial temperature to temperature of the measurements. The temperature of the generator column must be lower than initial gas temperature in order to make sure about the saturation of the gas with octanol. Then gas was passed through the glass wool generator column. In the final step, the chemicals in the gas phase were collected on an adsorbent trap. Due to the ability of the measurement of K_{OA} of the SVOCs by generator column method in the temperature range of -10°C to 45°C (Shoeib and Harner 2002, Harner and Mackay 1995, Harner

and Shoeib 2002). It is possible to measure K_{OA} values directly in the environmentally related temperature range with generator column technique.

The generator column method was suggested by Harner and Mackay (1995) to measure K_{OA} of the hydrophobic compounds because they were not intent to be in the aqueous solution. Hence there are some disadvantages of the generator column method such as it takes long times, experiments have several steps that can cause possible errors in the measurements and the extraction of the compounds from the traps is difficult. The gas chromatographic (GC) retention time method is an indirect method used for the determination of octanol-air partition coefficients as a function of temperature. Wania et al., (2002) used GC retention time method for the determination of the K_{OA} values of the nonpolar semivolatile organic compounds for the first time. In this method the retention times of the reference and the selected compound on a GC column and the temperature dependent K_{OA} values of the reference compound were used in the correlations for the estimation of the K_{OA} values of the selected compounds. After the study of the Wania et al., (2002), GC retention time method was used to determine the K_{OA} values of the various semivolatile organic compounds such as PCBs, PAHs, and PBBs (Wania et al., 2002, Hu et al., 2011, Odabasi et al., 2006). The GC retention time method is preferred because it is more simple and needs less time rather than the generator column method. In this study, the GC retention time method was used to determine the K_{OA} values of the SMCs as a function of temperature.

Gas saturation and effusion methods are the direct methods while GC retention time method is defined as indirect method for determination of SVOCs vapor pressures. The vapor pressures of the compounds lower than 10^2 Pa can be measured by gas saturation method at ambient temperature ranges (Sonnenfeld et al., 1983). In the gas saturation method a saturated gas phase is formed with an inert gas passing through a column containing the compounds for the analysis. The compounds are collected from the saturated vapor with a suitable technique, then analyzed using gas chromatography. Sonnenfeld et al., (1983) used gas saturation method for the determination of polynuclear aromatic hydrocarbons in the ambient temperature range from 10°C to 50°C . The reported vapor pressure values were 2.8×10^{-5} Pa to 10.4 Pa for PAHs. While direct methods give the vapor pressure of the substances in the solid state, GC retention time method directly gives the supercooled liquid vapor pressures of the compounds of interest. Jensen and Schall (1966) developed this technique to determine the vapor pressures of some phenoxyacetic herbicides. The temperature range of the

measurements were between 170 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ and the data obtained from the GC measurements were regressed to 25 $^{\circ}\text{C}$. Later this method was used commonly for the determination of various semivolatile organic compounds such as PAHs, OCPs, PBDEs (Odabasi et al., 2006, Zhang et al., 2009, Wong et al., 2000). Similar to the determination of K_{OA} , a reference compound with known vapor pressure values at the selected temperature range was used to correlate the retention time ratios and the logarithm of the supercooled liquid vapor pressure.

CHAPTER 3

MATERIALS AND METHODS

3.1. Experimental

3.1.1. Chemicals and Materials

The synthetic musk standard Musk-Mix 11 containing 1,2,3,5,6,7-Hexahydro-1,1,2,3,3 pentamethyl-4H-inden-4-one (Cashmeran, DPMI), 4-acetyl-1,1-dimethyl-6-tertbutylindan (Celestolide, ADBI), 6-acetyl- 1,1,2,3,3,5-hexamethylindan (Phantolide, AHMI), 5-acetyl-1,1,2,6-tetramethyl-3-iso-propylindan (Traseolide, ATII), 7-acetyl-1,1,3,4,4,6 hexamethyl 1,2,3,4 tetrahydronaphthalene (Tonalide, AHTN), and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2 benzopyran (Galaxolide, HHCB), Musk Ambrette (MA), Musk Ketone (MK), Musk Xylene (MX), Musk Moskene (MM), Musk Tibetene (MT) were purchased from Neochemia GmbH & Co.KG (Bodenheim,Germany). Gas chromatographic grade of ethyl acetate, acetone, n-hexane and dichloromethane (Suprasolv; Merck, Germany) were used for the clean up, extraction and GC-MS applications. Florisil (100–200 mesh; Sigma-Aldrich, USA) and anhydrous sodium sulfate (Fluka, Steinheim, Germany) were used after the extraction procedure of the indoor air samples in order to clean-up of pesticide residues, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), chlorinated hydrocarbons, aromatic compounds, fat, oil, waxes, and separation of nitrogen compounds from hydrocarbons (EPA 2007).

3.1.2. Determination of K_{OA} and P_L by GC-MS Technique

GC retention time method was used to determine the octanol-air partition coefficients and supercooled liquid vapor pressures of 11 synthetic musk compounds. A gas chromatograph (Thermo, Trace GC Ultra) coupled to a mass selective detector (Thermo DSQII) with electron impact ionization (GC/EI-MS) operated in selective ion monitoring (SIM) mode was used to determine the isothermal retention times of SMCs.

A 30-m 5% phenyl methyl siloxane capillary column (HP-5MS; 250 μm I.D., 0.25 μm film thickness) was used. Prepared samples, containing the synthetic musk compounds and the reference compound of pyrene, were injected at ten different temperatures for the determination of octanol-air partition coefficients and five temperatures were used to obtain supercooled liquid vapor pressures. High purity helium with 1 ml/min flow rate was used as carrier gas.

3.1.3. Collection and Preparation of Air Samples

The gas phase samples were collected on the phase which consists of polyurethane foam (PUF) cartridges and Amberlite XAD₂ resin (Supelco, Bellefonte, USA) sandwiched between PUF in a glass holder. Particulate phase samples were collected with glass fiber filters (Pall, Type A/E, Ø 37 mm, pores 1 μm).

3.1.3.1. Polyurethane Foam Filters (PUF)

Before the collection of samples PUFs were cleaned by ultrasonic extraction with dichloromethane and acetone:hexane mixture (1:1), followed by dichloromethane for an hour and again acetone:hexane mixture for an hour. After extraction, PUFs were wrapped aluminum foil loosely and dried at 60 °C for 3 hours in an oven, then kept in a jar with teflon lids prior use.

3.1.3.2. Glass Fiber Filters (GFF)

Glass fiber filters were baked overnight at 450 °C in an oven to remove the organic background contaminations. They were kept and stored in dessicator until sampling.

3.1.3.3. XAD₂ Resin

XAD₂ resin was cleaned by ultrasonic extraction with dicholoromethane for an hour and acetone an hour. After drying in an oven, resin was stored in glass jars with a teflon-lined lids.

3.1.3.4. Glassware

The glassware used in experiments were washed first with Alconox detergent and then Ultrapure chemical-free MilliQ (Millipore Elix-5) water. After washing, they were rinsed with primarily polar solvent aceton after apolar solvent hexane. They were left in an oven at 110 °C for 4 hour. All glassware were wrapped with aliminium foil and kept until use.

3.1.4. Sampling

Two types of sampling were conducted in the indoor environment of a university canteen for ten days in summer season. Gas and particulate SMCs collection on the filter and PUF and the total suspended particles for the determination of organic fraction part in indoor air. Gas and particulate phase samples were collected with an active sampling system consisted of a Harvard impactor (Air Diagnostics & Engineering Inc., Harrison, ME, USA). 37 mm glass fiber filter (1 μ m pore) was placed in the impactor to hold the particulate matter. Serially attached two glass cylinders containing gas sampling media were connected to the impactor for gas phase sampling. While front cylinder was consisted of PUF-resin-PUF, back cylinder contained only PUF and used for the detection of any breakthrough of gas phase SMCs. A vacuum pump (Air Diagnostics & Engineering Inc., SP-280) was connected finally to the PUF cartridges to left the collected air from the system. Sampling time was 7 hours with a 20 L/min of flow rate. At the begining and end of the sampling the pump was calibrated using a flow meter (Defender 510-H; BIOS, Buttler, NJ, USA). For the determination of organic fractioning the total suspended particle (TSP), another pump was used for the

sampling. The filters collected in this part were prepared for the use and weighted before and after sampling to find out particulate matter and its organic fraction.

3.1.5. Sample Extraction, Concentration and Clean-up

The extraction procedure was adapted from Peck and Hornbuckle (2006) for the synthetic musk compounds. Each of the gas and particulate phase samples (PUF, resin, GFFs) were extracted by acetone and hexane (1:1) mixture ultrasonically. Then the extracts were evaporated to reduce the volume to 5 ml under the gentle stream of nitrogen gas (100 ml/min). Following the reduction of volume, solvent exchange procedure was applied by adding 10 ml hexane for three times to exchange solvent into hexane. Finally, the extract was concentrated 2 ml volume. Aflorisil column was used for clean-up the sample. A piece of glass wool, 0.75 g florisil and 1 cm sodium anhydrous sulfate were placed in a pasteur glass pipet to enhance SMCs in column, respectively. Before column chromatography, florisil was activated at 650 $^{\circ}\text{C}$ while sodium anhydrous sulfate was activated at 450 $^{\circ}\text{C}$ in the oven. 37.5 μl water was added to 0.75 gr florisil in the column for deactivation. The samples were passed through the columns and discharged. 4 ml ethyl acetate were passed through the column and this solvent phase was collected in a 40 ml amber vial. Later again samples volume were reduced to 1 ml with nitrogen gas stream and solvent was changed into the hexane and this extracts were kept in the freezer until GC/MS analysis.

3.1.6. Determination of Concentrations

The analysis of the six polycyclic and five nitromusk compounds was done by a gas chromatography (Thermo, Trace GC Ultra, Austin, TX, USA) coupled to a mass selective detector (Thermo DSQII) with electron impact ionization operated in selective ion monitoring (SIM) mode. A 30-m 5% phenyl methyl siloxane capillary column (TR-5MS; 0.25 mm I.D., 0.25 μm film thickness) was used. For the injection of the samples programmable temperature vaporizer (PTV) port in splitless mode with a splitless time of 1 min was used. The carrier gas, helium, flow rate was 1 ml/min in the column. An oven temperature program composed of ramps was preferred due to the necessity of slow temperature gradients for the simultaneous analysis of the SMCs (Peck and Hornbuckle 2006). The ramps were run by keeping the oven temperature at 60 $^{\circ}\text{C}$ for 1 min, then, ramped to 180 $^{\circ}\text{C}$ at a rate of 15 $^{\circ}\text{C}/\text{min}$. Afterwards temperature increased

with a rate of 0.2 $^{\circ}\text{C}/\text{min}$ up to 183 $^{\circ}\text{C}$. The final temperature was 250 $^{\circ}\text{C}$ and held for 4 minutes. The ion source and MS transfer line temperatures were 230 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$, respectively. The retention times and quantifying ions for the synthetic musk compounds were shown in Table 3.1.

Table 3.1. Retention times and quantifying ions of synthetic musk compounds

Compound	Retention Time(min)	Ions
DPMI	9.92	191, 206
ADBI	12.73	229, 244
AHMI	13.59	229, 244
MA	15.55	253, 268
ATII	15.86	215, 258
HHCB	16.10	213, 243
MX	16.34	282, 297
AHTN	16.28	243, 258
MM	17.08	263, 278
MT	19.10	251, 266
MK	20.94	279, 294

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Octanol-Air Partition Coefficients (K_{OA})

The octanol-air partition coefficient (K_{OA}) is defined as the ratio of the compounds in octanol and air at equilibrium. K_{OA} describes the partitioning between air and organic phases in the environment such as plants, soil and organic part of the particles in the air. It is important to know the temperature dependent values of K_{OA} to investigate the partitioning process successfully between air and organic phases. Although direct method used to measure K_{OA} values is better, due to time consumption, running in a short temperature range and possible problems originates from the extraction procedure, GC retention time method is more preferable. It is an indirect method used to determine the K_{OA} values of SVOCs as a function of temperature. Because of its simplicity, it was preferred for the determination of K_{OA} values of the PAHs, PBDEs and OCPs (Wania et al., 2002, Odabasi et al., 2006, Zhang et al., 2009).

The K_{OA} values were obtained by GC retention time method explained in the study of Wania et al., (2002). It is known that the retention time of a compound (t_R) is directly proportional to the partition coefficient between the stationary phase and the gas phase (K_{SG}) on a GC column. The retention time ratios for a compound (i) and a reference compound are equal to the partition coefficient ratios for the same compound and the reference compound on the same GC column (equation (4.1)).

$$t_{Ri}/t_{R\text{ref}} = K_{SGi}/K_{SG\text{ref}} \quad (4.1)$$

When the phases are selected as octanol and air, based on the assumption that the ratio of the activity coefficients of compound i and of the reference compound in octanol ($\zeta_{OCTi}/\zeta_{OCT\text{ref}}$) is equal to the ratio of the activity coefficients of these two compounds in the stationary phase ($\zeta_{Si}/\zeta_{S\text{ref}}$). As a result, the equilibrium partitioning between stationary and gas phase can be similar to the partitioning between octanol and air.

$$\zeta_{OCTi}/\zeta_{OCTref} = \zeta_{Si}/\zeta_{Sref} \quad (4.2)$$

The equality of the equilibrium partition coefficients can be written as :

$$K_{OAi}/K_{OAre} = K_{SGi}/K_{SGref} \quad (4.3)$$

combining the equation (4.2) and (4.3), K_{OA} ratio of a compound i and of a reference compound is equal to their retention time ratio.

$$K_{OAi}/K_{OAre} = t_{Ri}/t_{Rref} \quad (4.4)$$

Integrating the Van't Hoff Equation that express the temperature dependence of K_{OA} and equation (4.4), Wania et al., (2002) derived the equation (4.5) and equation (4.6).

$$\ln K_{OAi} = (\Delta U_{OAi}/\Delta U_{OAre}) \ln K_{OAre} + C \quad (4.5)$$

$$\ln(t_{Ri}/t_{Rref}) = [(\Delta U_{OAi}/\Delta U_{OAre}) - 1] \ln K_{OAre} + C \quad (4.6)$$

where ΔU_{OA} (kJmol⁻¹) is the internal energy of phase transfer between octanol and air and C is the integration constant. The energies of phase transfer are assumed to be independent of temperature in the temperature range of GC measurements to environmentally related range. Using slope $S = [(\Delta U_{OAi}/\Delta U_{OAre}) - 1]$ and intercept C of the plot of $\ln(t_{Ri}/t_{Rref})$ versus $\ln K_{OAre}$ (Figure 2, 3), the octanol-air partition coefficients of the selected synthetic musk compounds were calculated from the equation (4.6).

In this study pyrene was selected as the reference compound due to its common use for many SVOCs in GC retention time method and its behaviour was similar to SMCs on the same GC column. K_{OAre} was stated as the octanol-air partition coefficient of the pyrene at selected temperatures. K_{OAre} values at isothermal tempertures were obtained from the equation (4.7) which was generated from the measured K_{OA} values of pyrene using generator column by Harner and Bidleman (1998) as a function of temperature.

$$\log K_{OA} = -4.56 + 3985(T, K)^{-1}, \quad r^2 = 0.990 \quad (4.7)$$

The $\log K_{OA}$ of SMCs at 25^0C were calculated based on the temperature regressions:

$$\log K_{OA} = A + B/(T, K) \quad (4.8)$$

The intercepts (A), slopes (B) of the temperature regressions and determined $\log K_{OA}$ of SMCs are listed in Table 4.1. ΔU_{OA} (the internal energies of phase transfer between octanol and air) were calculated as $2.303BR$ using the B (slope of the Equation 4.8), R (ideal gas constant). Calculated ΔU_{OA} values were also listed in Table 4.1.

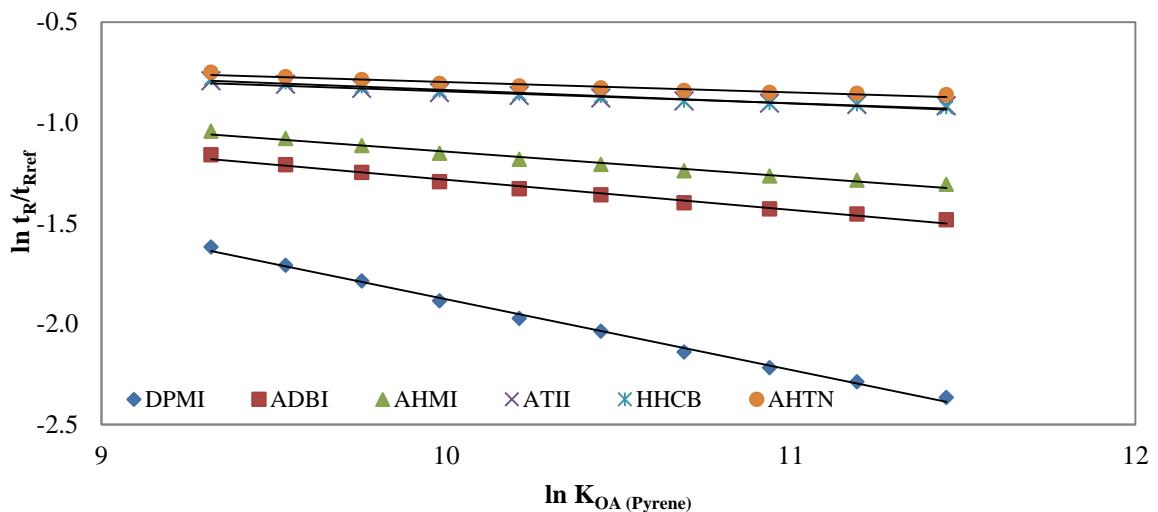


Figure 4.1. The relationships between the logarithm of the ratio of the retention times of polycyclic musks to the retention time of the standard reference compound (pyrene) and the $\ln K_{OA}$ of pyrene

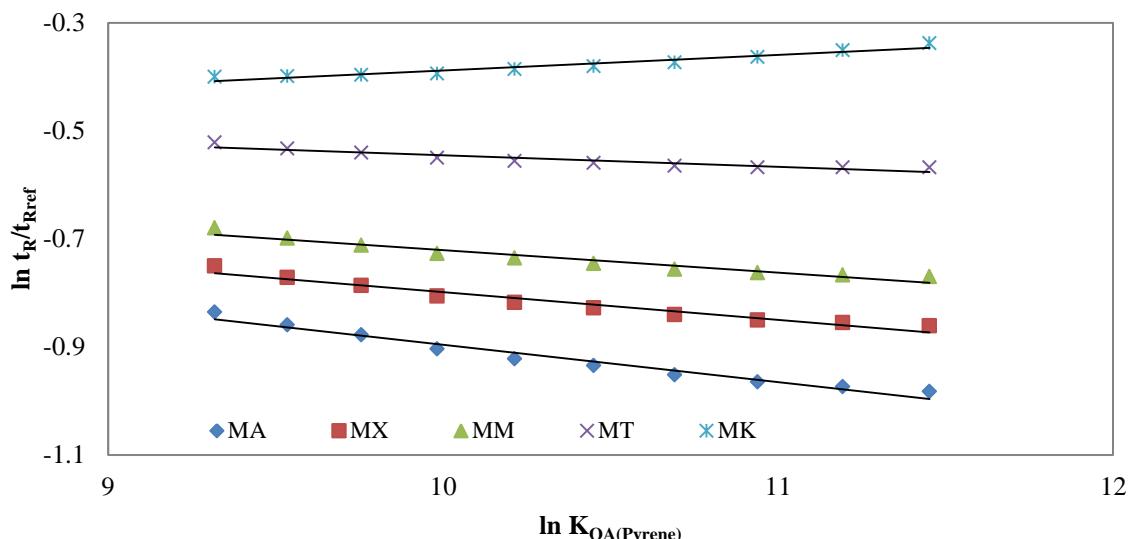


Figure 4.2. The relationships between the logarithm of the ratio of the retention times of nitromusks to the retention time of the standard reference compound (pyrene) and the $\ln K_{OA}$ of pyrene

The slopes of the correlations were different from each other for all polycyclic and nitro musks as seen in Figures 4.1 and 4.2, implying that the internal energy of phase transfer (ΔU_{OA}) is different for each compound due to the fact that the slope is the ratio of the internal energy of the phase transfer for the compound and the reference compound pyrene.

Odabasi et al., (2006) determined K_{OA} for PAHs as function of temperature with GC retention time method. Pyrene was used as reference compound in the measurements. The regressed log K_{OA} values were ranged from 6.24 to 12.48 for PAHs at 25 $^{\circ}\text{C}$. The ΔU_{OA} values were also ranged from 47.4 (kJ/mol) to 111.7 (kJ/mol). Zhang et al., (2009) studied with the another semivolatile organic compound class of OCPs. K_{OA} values of OCPs were obtained with GC retention time method as a function of temperature and regressed to 25 $^{\circ}\text{C}$. The range of the K_{OA} values changed between 7.50 and 9.58 and the ΔU_{OA} values were ranged from 66.6 (kJ/mol) to 86.4 (kJ/mol). The K_{OA} of PBDEs were also determined by GC retention time method using p,p'-DDT as reference compound by Wania et al., (2002). The obtained K_{OA} range for PBDEs was between 7.34 and 11.78 while the ΔU_{OA} values were ranged from 61.9 (kJ/mol) to 105.7 (kJ/mol). Although all of the studies mentioned above also used directly measured K_{OA} values of the selected compounds to calibrate the results taken from the GC analysis, in this study, the results were not calibrated because there was no directly

measured value for any SMC reported in the literature. For SMCs the $\log K_{OA}$ at 25 $^{\circ}\text{C}$ ranged from 6.42 to 8.77 and the ΔU_{OA} values ranged from 49.5 to 78.5 as shown in Table 4.1. When SMCs were compared with the other semivolatile organic compounds, they were nearly in the same range both for K_{OA} and ΔU_{OA} . As there were no study about the octanol-air partition coefficients of the SMCs, experimental determinations should be done to evaluate the validity of the K_{OA} values obtained from GC retention time method in this study.

Table 4.1. Calculated octanol-air partition coefficients, regression parameters (B,A) and phase transfer energies at 25 $^{\circ}\text{C}$

Compound	$\log K_{OA}$	B	A	$\Delta U_{OA}(\text{kJ/mol})$
Cashmeran (DPMI)	6.43 \pm 0.202	2585	-2.24	49.5 \pm 0.1
Celestolide (ADBI)	7.58 \pm 0.265	3388	-3.78	64.9 \pm 0.1
Phantolide (AHMI)	7.76 \pm 0.273	3490	-3.95	66.8 \pm 0.1
Traseolide (ATII)	8.18 \pm 0.293	3750	-4.40	71.8 \pm 0.1
Galaxolide (HHCB)	8.15 \pm 0.291	3718	-4.33	71.2 \pm 0.1
Tonalide (AHTN)	8.24 \pm 0.296	3781	-4.45	72.4 \pm 0.1
Musk ambrette (MA)	8.11 \pm 0.290	3710	-4.33	71.0 \pm 0.1
Musk xylene (MX)	8.24 \pm 0.296	3781	-4.45	72.4 \pm 0.1
Musk moskene (MM)	8.31 \pm 0.299	3819	-4.50	73.1 \pm 0.1
Musk tibetene (MT)	8.48 \pm 0.305	3900	-4.61	74.7 \pm 0.1
Musk ketone (MK)	8.77 \pm 0.321	4101	-4.99	78.5 \pm 0.1

4.2. Determination of the supercooled liquid vapor pressures

The supercooled liquid vapor pressures (P_L) for the synthetic musk compounds were also determined from the GC retention time method that used by Lei et al., (2002) and Wong et al., (2000). The supercooled liquid vapor pressures at the selected temperatures were calculated from the equation (4.9).

$$\ln P_L = (\Delta H_{vap}/\Delta H_{vap-ref}) \ln P_{Lref} + C \quad (4.9)$$

where ΔH_{vap} , $\Delta H_{vap-ref}$ (kJmol⁻¹) are the enthalpy of vaporization of the compound and the reference compound pyrene, respectively. P_{Lref} (Pa) is the vapor pressure of the reference compound pyrene. In the equation (4.9), the ratio of the enthalpy of vaporization was assumed to be constant between the temperature range of the GC measurements and the reported temperature 25⁰C (Lei et al., 2002). $(\Delta H_{vap}/\Delta H_{vap-ref})$ ratio and the constant C, were obtained from equation (4.10).

$$\ln(t_{Ri}/t_{Rref}) = [1 - (\Delta H_{vap}/\Delta H_{vap-ref})] \ln P_{Lref} - C \quad (4.10)$$

where (t_{Ri}/t_{Rref}) is the logarithm of the isothermal GC retention time ratio of the compound and pyrene at the studied temperature range. The infinite dilution activity coefficients are assumed as the same for the compound and the reference compound in the stationary phase derived from the equation (4.10) (Lei et al., 2002).

Pyrene was used as a reference compound by Lei et al., (2002), for the determination of supercooled liquid vapor pressures of the polycyclic aromatic hydrocarbons. The selection of the reference compounds based on the availability of the temperature dependent solid and liquid vapor pressures to plot the correlation between the retention time ratio and supercooled liquid vapor pressure of the reference compound (Figure 4.3, 4.4). It is also pointed out that the vapor pressures of the reference compound should be selected from the data obtained by the experimental methods. Růžička et al., (2012) reported that the vapor pressure data for the reference compound determined by direct methods should be used measured by direct methods for the extrapolation to improve the success of the GC retention time technique. The vapor pressure data obtained by the extrapolation of the data determined by the GC retention time technique should not be used if the vapor pressure data obtained from direct methods are attained (Růžička et al., 2012).

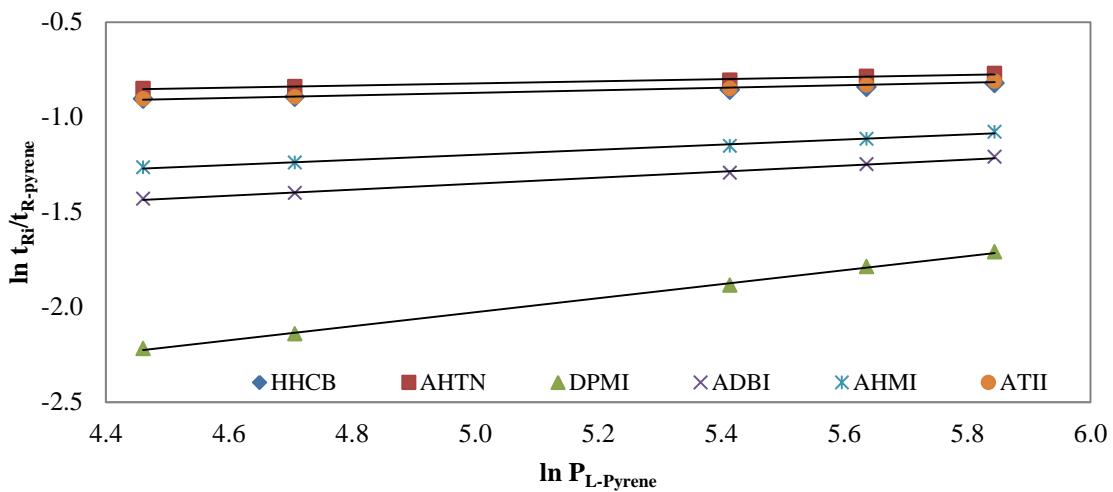


Figure 4.3. The relationship between $\ln(t_{Ri}/t_{R\text{ref}})$ and $\ln P_{L\text{-Pyrene}}$ for polycyclic musk compounds

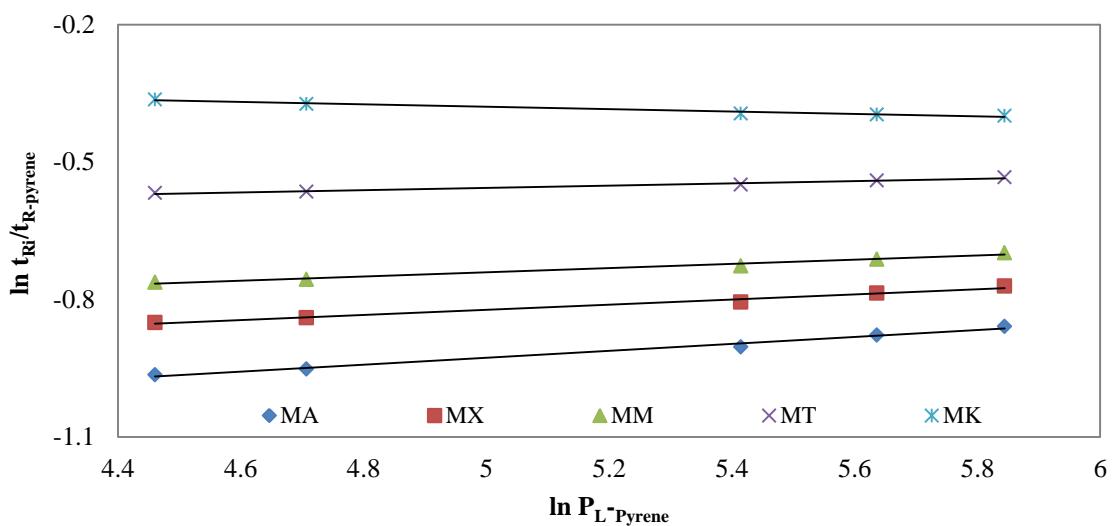


Figure 4.4. The relationship between $\ln(t_{Ri}/t_{R\text{ref}})$ and $\ln P_{L\text{-Pyrene}}$ for nitromusk compounds

While the errors come from the GC retention time method because of the assumptions in the calculations become larger after the extrapolation. In this study, the values of temperature dependent vapor pressure of pyrene determined by inclined-piston-gauge manometry reported by Smith et al., (1980) were used in the determination of the supercooled liquid vapor pressures of SMCs in both Cox and Clasius-Clapeyron regressions. The vapor pressures of SMCs obtained by the GC retention time method at 155^0C , 160^0C , 175^0C , 180^0C and 185^0C temperatures isothermally, were regressed to

25⁰C with Cox and Clasius-Clapeyron equations. In the Cox regression analysis equation (4.11) was used as the model:

$$\ln P_R = (1 - (1/T_R)) \exp(A + BT_R + CT_R^2) \quad (4.11)$$

where P_R , is the ratio of the pressure at the stated temperature(P) and the pressure of the compound at normal boiling point (P_0). The ratio of the selected temperature and the normal boiling temperature is shown as T_R . A,B and C are the parameters of the Cox regression model and they were listed in Table 6. for all SMCs.

Table 4.2. Parameters of the Cox Equation (equation (4.11))

SMC	A	B	C
HHCB	2.798041826	-0.56396	0.664871776
AHTN	2.900695	-0.75204	0.411053
DPMI	7.86976247	-15.1277	11.04338
ADBI	2.566828	-0.44349	0.942024
AHMI	4.616939	-5.8107	4.216893
MA	2.911574	-0.83301	0.323727
ATII	4.225065	-4.53226	3.165388
MX	2.974505	-0.9717	0.164951
MM	4.219557	-4.45841	3.104539
MT	2.988126	-0.93753	0.201121
MK	3.019158	-0.82357	0.28481

The normal boiling points of SMCs used in the equation (4.11) were also listed in Table 2.1. The normal boiling point corresponds to the temperature that the pressure is equal to 101.325 kPa at this point. The log P_L values of SMCs were obtained from Cox regression at 25⁰C ranged from 0.52 to -4.53.

The extrapolation with Clasius-Clapeyron equation was also conducted to obtain the vapor pressures of SMCs at 25⁰C. Equation (4.12) was used for the regressions where, m and b are the slope and the constant, respectively. The log P_L values obtained from the regression using Clasius-Clapeyron equation ranged from 0.36 to -2.04.

$$\log P_L(\text{Pa}) = m(T, \text{K})^{-1} + b \quad (4.12)$$

In the Clasius-Clapeyron equation the enthalpy of vaporization (ΔH) is assumed to be constant and this approximation is only valid over short temperature ranges, for

example the pressure values obtained by the effusion method (Růžička et al., 2012). So over an extended temperature range the regression equations require three or more parameters. Scott and Osborn (1979) used Cox equation for the estimation of vapor pressure and got the best result in extrapolation for n-decane. Afterwards the deviations of the regression equations were calculated by Růžička et al., (2012). as 1.6 %, 14 % and over 100 % for Cox equation, Antoine equation and Clasius-Clapeyron equation, respectively. It was recommended that the use of the high quality data obtained by experimental methods eliminates the significant errors (Růžička et al., 2012). Therefore, the vapor pressure values obtained from GC retention time method was extrapolated by using Cox equation as well.

The experimentally determined vapor pressure values for HHCB and AHTN by Balk and Ford (1999) at room tempertaure were used for comparison with this study. Gas saturation method with respect to OECD Test Guideline 104 was used to obtain the vapor pressures and they were reported 0.0682 and 0.0727 Pa for AHTN and HHCB, respectively (Balk and Ford 1999). The other reported vapor pressure values for SMCs in literature were obtained by estimation method. Paasivirta et al., (2002) determined temperature dependent vapor pressures for SMCs using a Clasius-Clapeyron type equation and estimate the coefficients of equation by the modified Watson method. The comparison of the vapor pressure values with available values in literature showed that the values with Cox regression were deviated 24 % and 50 % from the experimental values, respectively. Similarly calculated deviations from the Clasius-Clapeyron equation were 29% for HHCB and 50% for AHTN. The maximum deviations were obtained from modified Watson method. They found out significant correlation with literature for the estimated parameters and HPLC-derived values, but a great deviations, especially in log Kow (octanol-water partition coefficient) values.

Table 4.3. The log P_L values of the SMCs determined by experimental, Cox, Clasius-Clapeyron and modified Watson method at 25°C

Compound	Experimental	Cox Equation	Clasius-Clapeyron Equation	Modified Watson Method ^b	
				P_S	P_L
HHCB	-1.14 ^a	-1.41	-1.47	-10.75	-7.56
AHTN	-1.17 ^a	-1.75	-1.49	-12.61	-8.84
DPMI	-	-4.53	0.36	-14.55	-9.39
ADBI	-	-0.78	-0.83	-12.22	-7.85
AHMI	-	-2.00	-1.00	-12.13	-8.56
MA	-	-0.77	-1.43	-13.00	-9.14
ATII	-	-1.89	-1.43	-10.27	-8.71
MX	-	-0.52	-1.49	-13.79	-9.64
MM	-	-2.00	-1.58	-14.35	-10.36
MT	-	-0.74	-1.75	-14.60	-10.58
MK	-	-1.40	-2.04	-14.61	-9.93

a.Balk and Ford (1999)

b.Paasivirta et al., (2002)

4.3. Concentrations of Synthetic Musk Compounds in the University Cafeteria

4.3.1. Concentrations of Synthetic Musk Compounds in the Gas Phase

The measured average gas phase concentrations ranged from 0.27 ng/m³ to 106.8 ng/m³ (Table 4.4) in the university canteen. All of the compounds were detected in the gas phase in the order of HHCB > MK > ADBI > AHTN > ATII > DPMI > MX > AHMI > MM > MT > MA from the highest to the lowest concentration values. The presence and levels of SMCs in indoor depend on the use of cleaning agent in specific locations and people who use personal care products present during the sampling.

Kallenborn and Gatermann (2004) measured concentrations of SMCs in the cafeteria of the Norwegian Institute for Air Research. In this study HHCB, AHTN and ATII was detected at the levels 35.3 ng/m³, 11.6 ng/m³ and 4.8 ng/m³, respectively. MX and MK were not found in the air samples. They also studied in the rest facilities in Norwegian Institute for Air Research. In rest facilities HHCB concentration was the highest with the level of 19 ng/m³ among the other SMCs. Unlike the results in cafeteria they found MX and MK in the rest facilities. The concentrations were 0.6 ng/m³ for MX and 0.2 ng/m³ for MK. In our detected levels MK concentration was

96.7 ng/m³ which was much higher, may be the result of the consumption of the perfumes, cleaning agents etc. containing MK.

Kallenborn and Gatermann (2004) were collected indoor air samples from laboratories, hair dresser and toilet. In hair dresser ATII level was 5.2 ng/m³ that is the closest result to our study which was 9.54 ng/m³ for ATII. All of the concentrations measured in various indoor environments were interestingly lower than this study. The changes of concentration mainly depend on the personnel care products or the other household products and the amount used in the indoor environment.

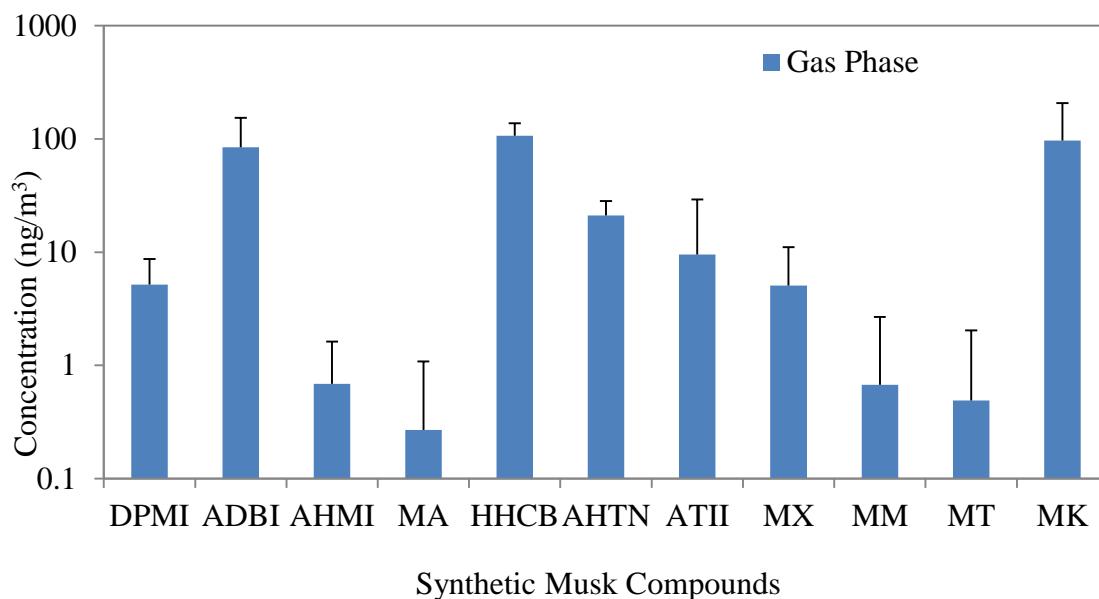


Figure 4.5. The gas phase concentrations of synthetic musk compounds in the university cafeteria

4.3.2. Particulate Phase Concentrations

SMCs concentrations were also measured for the particulate phase in the cafeteria. The average concentrations of DPMI, ADBI, ATII, MX and MK were in the range of 0.06 ng/m³ to 210.5 ng/m³ (Table 4.4). The highest concentration was determined for ADBI while the lowest concentration was found for ATII. AHMI, MA, HHCB, AHTN, MM, MT were not detected in any indoor particulate phase samples.

Sofuoğlu et al., (2010) measured indoor air particulate phase SMCs concentrations in a primary school classroom and a women's sport center. In the classroom HHCB and AHTN concentrations were reported as the highest

concentrations among the other SMCs while in this study HHCB and AHTN were not found in the particulate phase samples. This result may be explained by the dependency of the composition from the use of cleaning or personal products in the area. Although MK was found neither in classroom nor in sports center samples, in this study MK concentration was detected 64.3 ng/m^3 .

Indoor air particulate phase polycyclic musks concentrations was measured by Chen et al., (2007) in a cosmetic plant. SMCs concentrations were reported in the order from highest to lowest was HHCB> AHTN> DPMI> ADBI> AHMI in the workshop of the cosmetic plant. DPMI concentration was found 2.55 ng/m^3 that was higher than university canteen concentration. It is known that Turkey is a country importing different substances from India, China while European countries have some limitation for the use of nitromusk compounds.

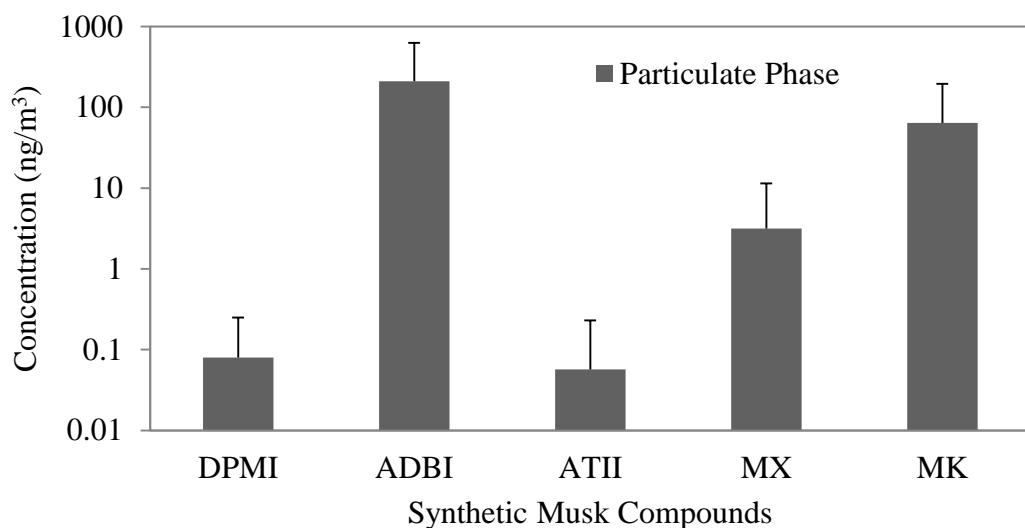


Figure 4.6. The levels detected in the particulate phase

The differences between the concentrations among the studies about the indoor air concentrations of the SMCs occur because of the variety of the ambient conditions.

4.3.3. Gas/Particle Distributions

Synthetic musk compounds were mainly found in the gas phase rather than particle phase as shown in Figure 4.7. AHMI, MA, HHCB, AHTN, MM, MT were totally detected in the gas phase. However ADBI and MK dominantly distributed in the particulate phase. For a further investigation gas-particle partitioning models were studied in the next part.

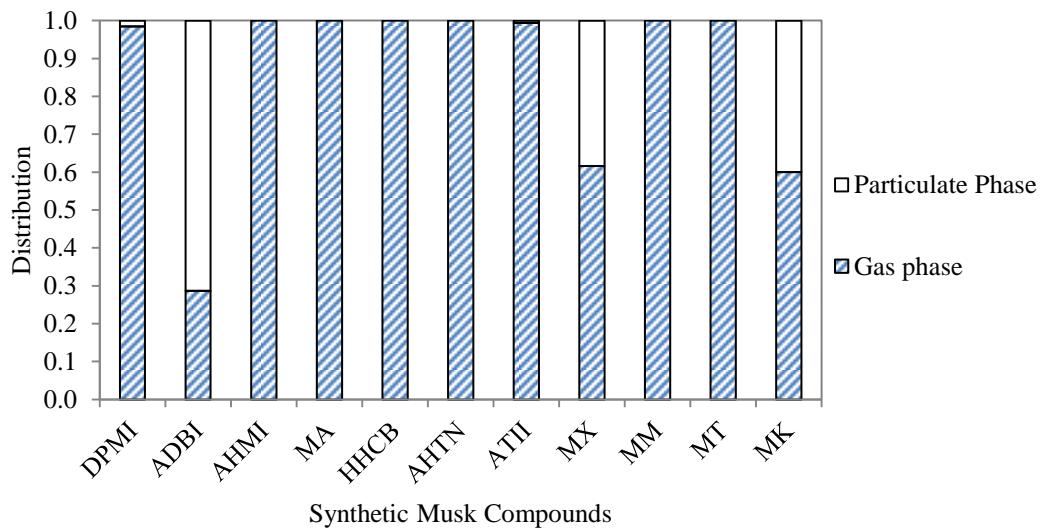


Figure 4.7. Gas and particulate phase distributions

Table 4.4. The mean concentrations(\pm standard deviation) of SMCs in the university cafeteria

SMC	Gas phase(ng/m ³)	Particulate phase(ng/m ³)
DPMI	5.15 \pm 3.53	0.08 \pm 0.17
ADBI	84.7 \pm 69.4	210.5 \pm 416.8
AHMI	0.69 \pm 0.94	-
MA	0.27 \pm 0.81	-
HHCB	106.8 \pm 30.5	-
AHTN	21.0 \pm 7.27	-
ATII	9.54 \pm 19.6	0.06 \pm 0.17
MX	5.07 \pm 6.00	3.15 \pm 8.25
MM	0.67 \pm 2.01	-
MT	0.49 \pm 1.55	-
MK	96.7 \pm 111	64.3 \pm 131

4.4. Gas-Particle Partitioning

4.4.1. Adsorption and Absorption Models

The adsorption process between the adsorbed molecules and the particle surface is complex and controlled by both physical and chemical forces. The adsorption characteristics of a surface for a particle are explained by adsorption isotherms where at constant temperature, the amount of the gas adsorbed on the surface depends on the gas partial pressure. Since the isotherms need experimentally determined information to explain the validity of the theory, the adsorption isotherms are not useful to investigate the adsorption processes (Seinfeld and Pandis 2012). Yamasaki et al., (1982) defined the gas-particle partitioning process by the parameter of partitioning coefficient K_p (equation 2.1). However K_p value is not able to explain partitioning in detail whether the process is adsorption, absorption or the combination of both. From the equation (2.1), it can be said that if the K_p value is larger, more organic matter exist in the particulate phase rather than the gas phase thus K_p is a function of total particulate matter. Pankow (1987) explained that for adsorption, the number of adsorption sites and the difference between the enthalpy of desorption and the enthalpy of volatilization must be constant for the similar compounds on the partitioning while the activity coefficients of the compounds must remain constant in absorption (Pankow 1991). Therefore, at equilibrium, the slope of the correlation between $\log K_p$ and $\log P_L$ should be near -1 with accepting the validity of the following assumptions for adsorption and absorption.

In this study, the gas-particle partitioning constant K_p was calculated from the equation 2.1. Total suspended particle (TSP) concentrations were ranged from 2.81 $\mu\text{g}/\text{m}^3$ to 45.67 $\mu\text{g}/\text{m}^3$ in sampling duration. K_p was calculated from the values of the gas and particulate phase concentrations of the SMCs for each day and the whole sampling time. The vapor pressures of the SMCs obtained in this study from the GC retention time method and regressed to 25 $^{\circ}\text{C}$ with Cox Equation were used to plot the $\log K_p$ - $\log P_L$ correlation.

The correlation between the $\log K_p$ and $\log P_L$ was found weak where the R^2 value was 0.052 and the slope of the correlation was -0.52 (Figure 4.8). It was expected

that at equilibrium, the slope for either adsorption or absorption should be close to -1. In our results, slope was far away from the value of -1 .

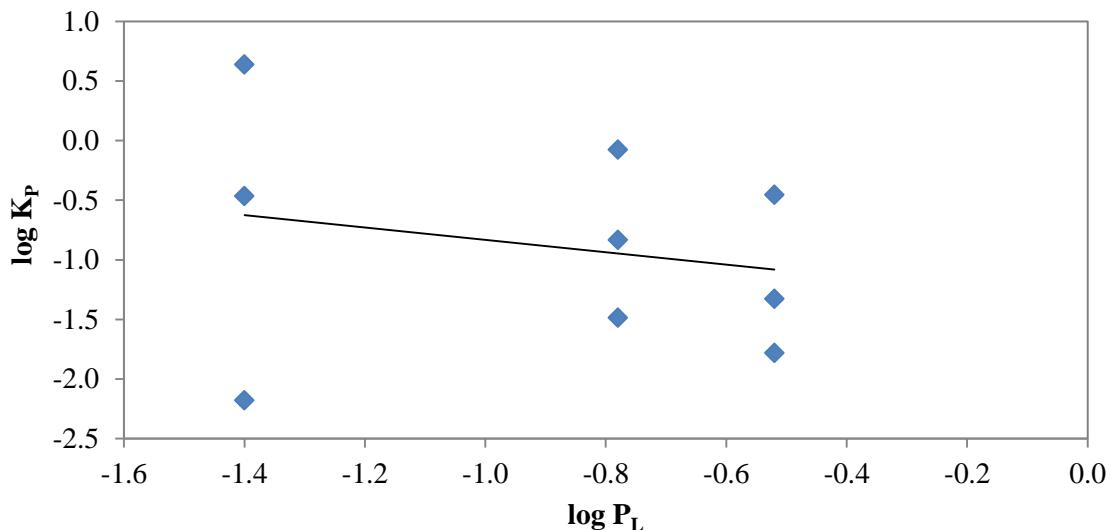


Figure 4.8. $\log K_p$ vs. $\log P_L$ of the samples

It was also difficult to draw the correlation by using very few sample because the particulate phase were not collected for most of the SMCs. The assumptions were not valid and the correlation between $\log K_p$ and $\log P_L$ was weak to decide the gas-particle partitioning process as adsorption for the SMCs and also this results were not sufficient to make true and valid comments.

The deviations for the slope value of -1 could originate as a result of several factors such as non-equilibrium (Pankow and Bidleman 1992), the variability of the differences between the enthalpies of desorption and volatilization (Pankow and Bidleman 1992), the changing numbers of available adsorption sites (Pankow and Bidleman 1992), non-exchangeability (Pankow 1991) and the changes in the stability of the activity coefficients of the compounds (Pankow 1994).

Non-exchangeability were reported as an important factor for PAHs because of their formation and being trapped inside particles after the combustion processes (Simcik et al., 1998), but it was reported that the slopes observed for PCBs less than -1 might not be important that they were directly emitted to the atmosphere as gases (He and Balasubramanian 2009). Like PCBs, SMCs are released to the atmosphere primarily as gases, so non-exchangeability might not cause to deviate the slope from -1 for SMCs.

The deviations might be due to the changing the numbers of available adsorption sites and it was reported to steric hindrance that depended on the surface irregularities could be a reason(Simcik et al., 1998). The stearically exclusion of the larger molecules caused shallower slope for PCBs than PAHs, because the molecular sizes of the PAHs were larger than PCBs (Simcik et al., 1998). Since the molecular sizes of the SMCs were smaller than PCBs and PAHs, the slopes might be shallower for this reason.

SMCs into organic matter, activity coefficients were also expected to be constant. The relationship between the octanol-air partition coefficients and the supercooled liquid vapor pressures can be used to investigate the validity of this assumption (Simcik et al., 1998). The relationship between the $\log K_{OA}$ and $\log P_L$ was shown in Figure 4.10 for the semivolatile organic compounds of PAHs, OCPs, PBDEs and SMCs. The K_{OA} and P_L values obtained by GC retention time method were used for all the compounds in the plot. According to Figure 4.10, the semivolatile organic compounds exhibited nearly same trend for the correlation between $\log K_{OA}$ and $\log P_L$. The slope of the correlation was found -0.967 as near to -1, it showed that the assumption of the activity coefficients remain constant was valid for SMCs. From this statement, the gas-particle partitioning process can be mentioned as absorption for SMCs.

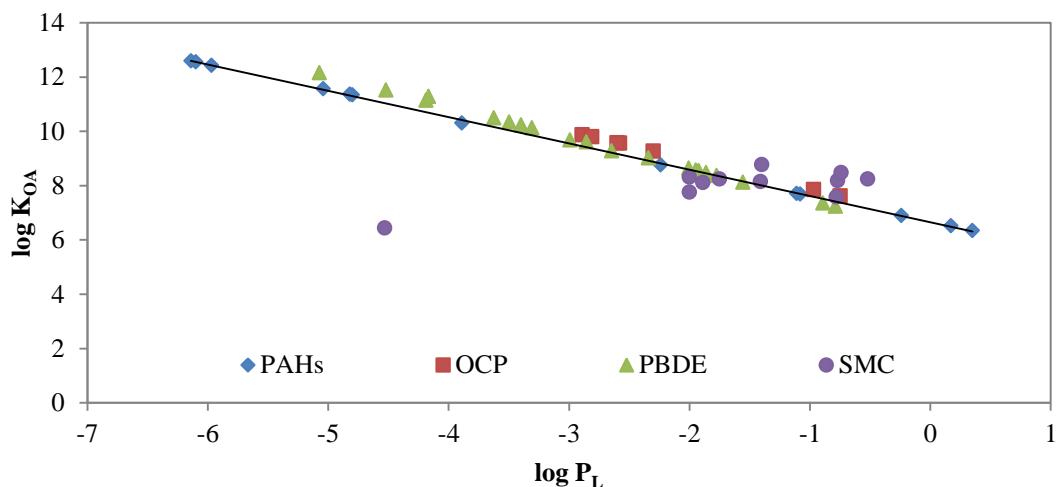


Figure 4.9. The relationship between $\log K_{OA}$ and $\log P_L$ for PAHs, OCP, PBDEs and SMCs.

In addition equation (4.13) derived by Xiao and Wania (2003) from the correlation between $\log K_{OA}$ and $\log P_L$ for 222 chemicals including PCBs, PBDEs,

PAHs etc. also used for the validation of the assumption of the stability of the activity coefficients.

$$\log K_{OA} = (-0.98784 \pm 0.00584) \log P_L + (6.6914 \pm 0.0171) \quad r^2 = 0.9924 \quad (4.13)$$

According to the equation (4.13), since the slope is close to -1 and the coefficient of the regression is high, the assumption that γ_{oct} remains constant was valid. The $\log P_L$ values for SMCs (in this study), PAHs Odabasi et al., (2006) and PBDEs from the study of Wong et al., (2000) were used to calculate $\log K_{OA}$ values by equation (4.13). Validity of activity coefficient being constant assumption was indicated again for SMCs and it can be reported that octanol might be a good indicator to reflect the mechanism of the absorption in the organic matter.

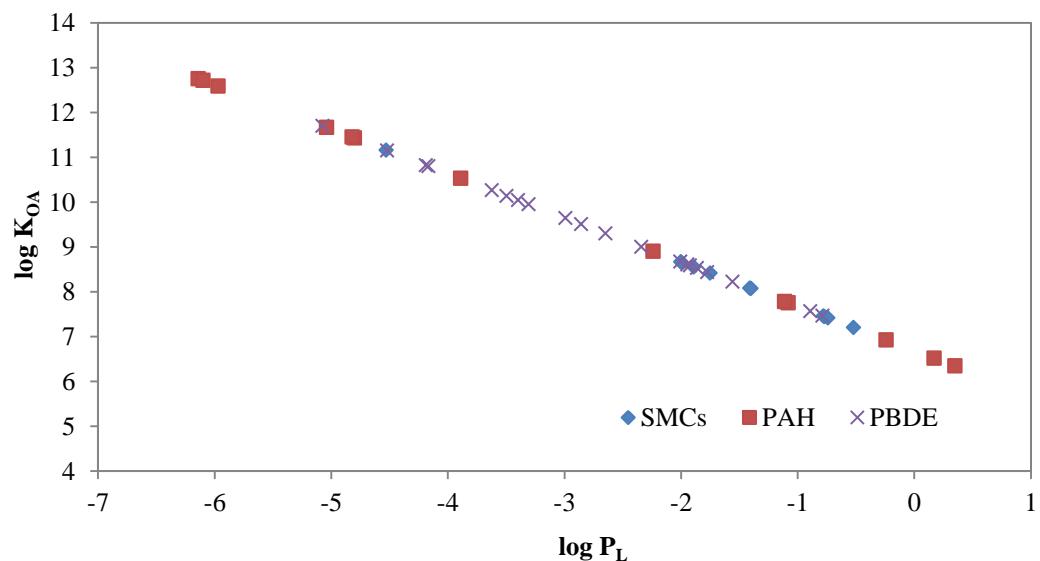


Figure 4.10. The correlation between $\log K_{OA}$ and $\log P_L$ for SMCs, PAHs and PBDEs.

Non-equilibrium also might cause the deviations for the slopes. The equilibration of the SMCs in the air may become slowly. Hence even at equilibrium, the deviations can be occur (Simcik et al., 1998).

Although the slope deviations were observed for the PAHs and PCBs, the coefficients of the determination for the plots were found higher than our results, showed that there was a good correlation between the K_p and P_L for the PAHs and PCBs

(Table 4.6). In order to obtain more reliable results for the relationship between K_p and P_L for adsorption of SMCs, the sampling duration should be increased for the collection of more particulate phase. Temperature measurements also should be conducted due to temperature dependency of gas-particle partitioning as a result of temperature dependence of vapor pressure. For the investigation of the effect of temperature, samples should be collected in different seasons.

Table 4.5. Slope and coefficient of determination (R^2) of SMC, PCB and PAH for log K_p -log P_L correlation

Compound	Slope	R^2	Reference
SMC	-0.52	0.052	This study
PCB	-0.58	0.78	He and Balasubramanian (2009)
PCB	-0.51	0.70	Simcik et al., (1998)
PCB	-0.56	0.86	Yeo et al., (2003)
PCB	-0.44	0.79	Mandalakis et al., (2002)
PCB	-0.42	0.79	Sıddık Cindoruk and Tasdemir (2007)
PAH	-0.76	0.81	He and Balasubramanian (2009)
PAH	-0.51	0.78	Mandalakis et al., (2002)
PAH	-0.69	0.78	Simcik et al., (1998)

4.4.2. K_{OA} Absorption Model

The octanol-air partition coefficients of SMCs obtained by GC retention time method in this study were used to obtain K_p (partition coefficient.) via K_{OA} . The calculated K_p values (equation (2.1)) resulted in $R^2= 0.387$ and slope=0.66, respectively.

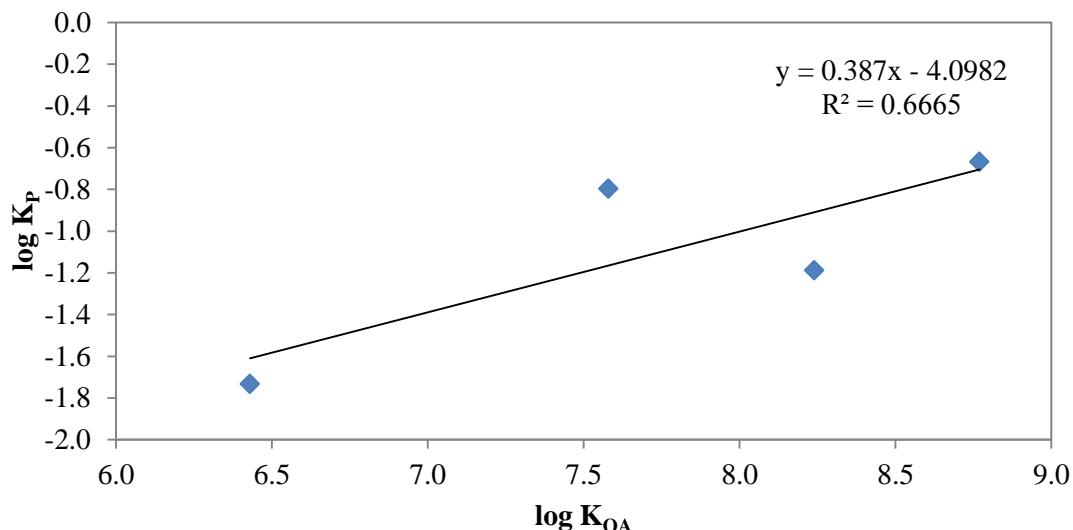


Figure 4.11. The correlation between $\log K_p$ and $\log K_{OA}$

K_p can be predicted from using octanol-air partition coefficient when the absorption process is assumed to be dominant in the partitioning (Harner and Bidleman 1998). The K_p values were calculated by equation 2.5 equation 2.5., if the fraction of the organic matter is known. The average fraction of the organic matter was found 0.2 from the difference between the weights of the glass fiber filters before and after the burning in the oven at 450 $^{\circ}C$, in this study. The calculated K_p values decreased depending upon the elution order in the GC column.

Table 4.6. Calculated $\log K_p$ values from the K_{OA} absorption model for the synthetic musk compounds

Compound	Modeled $\log K_p$
DPMI	-6.1982
ADBI	-5.0482
AHMI	-4.8682
MA	-4.4482
HHCB	-4.4782
AHTN	-4.3882
ATII	-4.5182
MX	-4.3882
MM	-4.3182
MT	-4.1482
MK	-3.8582

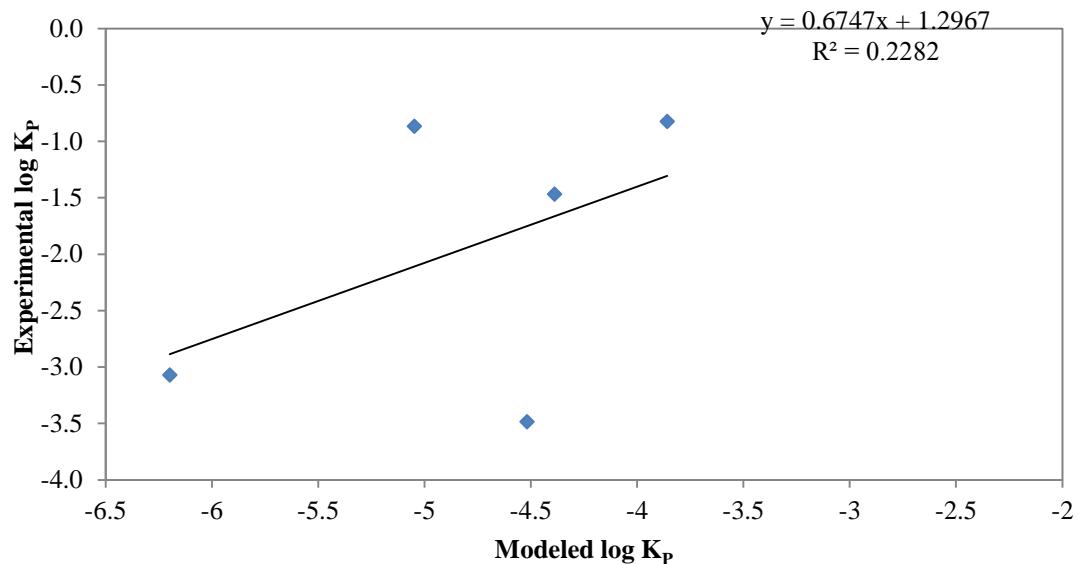


Figure 4.11. Correlation between the experimental log K_p and modeled log K_p

The organic matter fractions were chosen between 10% and 20% from the reported values for urban aerosols in K_{OA} absorption model. However He and Balasubramanian (2009) suggested that due to organic matter fractions dependency in sampling area in the ambient air will affect the partitioning, therefore, the measured *f_{OM}* values fits the data much better for the gas-particle partitioning of SVOCs. In this study, the measured average organic matter fraction was used in the K_{OA} absorption model. It could concluded that, K_{OA} seems a better predictor for gas-particle partitioning for SMCs, and the gas-particle partitioning process might be dominated by absorption.

The study conducted was not able to explain the relationship clearly. The more particulate and gas phase data are required to clear the picture. Therefore some outdoor air samples also should be collected for a comparison with the indoor air samples which should be collected where particle phases are present.

CHAPTER 5

CONCLUSION

Octanol-air partition coefficients (K_{OA}) and supercooled liquid vapor pressures (P_L) were determined using GC retention time method as a function of temperature, gas and particulate phase concentrations were measured in indoor air and gas-particle partitioning processes were also investigated for eleven synthetic musk compounds.

$\log K_{OA}$ values at 25 $^{\circ}\text{C}$ ranged from 6.42 to 8.77. $\log P_L$ values obtained from Cox Equation ranged from 0.52 to -4.53 while the values obtained from Clasius-Clapeyron Equation ranged from 0.36 to -2.04. All of the compounds were detected in the gas phase and the levels of SMCs in the order from the highest to the lowest concentration as MK > HHCB > ADBI > AHTN > ATII > DPMI > MX > AHMI > MM > MT > MA. In the particulate phase the highest concentration was determined for MK while the lowest concentration was found for ATII. AHMI, MA, HHCB, AHTN, MM, MT were not detected in any indoor particulate phase samples. Although AHMI, MA, HHCB, AHTN, MM, MT were totally existed in the gas phase, ADBI and MK dominantly distributed in the particulate phase. The correlation between gas-particle partitioning coefficient and P_L was found weak for the $\log K_p$ - $\log P_L$ model while K_{OA} should be a good descriptor for SMCs partitioning.

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