Summer 2014

Methamphetamine absorption by skin oils: accumulated mass, partition coefficients and the influence of fatty acids

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Department:

METHAMPHETAMINE ABSORPTION BY SKIN OILS: ACCUMULATED MASS, PARTITION COEFFICIENTS AND THE INFLUENCLE OF FATTY ACIDS

by

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A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN ENVIRONMETNAL ENGINEERING

2014

Approved by

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PUBLICATION THESIS OPTION

This thesis has been prepared in the style utilized by Atmospheric Environment. Pages 7 – 37 will be submitted for publication in this journal. The sections of Introduction, Goals and Objectives, Conclusions, Practical Implications, Future Research and the Appendix contain supplemental information for the journal article. They present some information required to complete this thesis but are not necessary for submission to the journal.

ABSTRACT

Occupants of former methamphetamine laboratories, often residences, may experience increased exposure through the accumulation of the methamphetamine in skin oil. The objectives of this study were to determine equilibrium partition coefficients of vapor-phase methamphetamine with artificial skin oil (ASO), artificial skin oil without fatty acids and real skin oil. A 10 L flow through stainless-steel chamber and in-line filter holders were used to expose skin-oil coated filters to vapor-phase methamphetamine at concentrations ranging from 12 ppb to 159 ppb and samples were analyzed for exposure time periods from 2 hours to 60 days. For a low vapor-phase methamphetamine concentration range of ~12-28 ppb, the equilibrium partition coefficient was 1499 ± 195 µg meth/g SO/ppb. For a high concentration range of 98-159 ppb, the equilibrium partition coefficient was lower, 394 ± 90.6 µg meth/g SO/ppb, suggesting some saturation of the available absorption capacity. The partition coefficient for artificial skin oil without fatty acids was 33 ± 6 µg meth/g SO/ppb, much lower than any value measured in this study or a previous 60 day study that used real human skin oil in which an average mass normalized partition coefficient of 1410 ± 840 µg meth/g SO/ppb was measured. We believe that the measured coefficients are much greater than the predicted value due to the presence of organic acids in the skin oil, which contribute protons, lower the pH and increase the capacity for basic organic compounds like methamphetamine. The very large absorption capacity suggests that surfaces covered in skin oils would accumulate methamphetamine to levels that exceed recommended surface remediation standards, even for air concentrations in the low part per trillion range.

ACKNOWLEDGEMENTS

I would like to thank Dr. Glenn Morrison, my advisor and mentor for helping me through the last two years. Without his support and guidance, I would not have been able to complete the research for this thesis. His patience and encouragement throughout this process have been immense and have allowed me to accomplish my goal of completing my master's program and this thesis.

I would also like to thank Dr. Joel Burken and Dr. Nuran Ercal for taking time out of their busy schedules to be a part of my committee. Thanks should also be extended to Dr. Honglan Shi for her assistance with the analytical instruments and the ERC for the use of the instruments. I also need to thank Gary Abbott, Hongwan Li, Melissa Buechlein and Brandon Pollpeter for their help during my research. Without each of these people and others in the department, I could not have completed this project.

Finally, I would like to thank Brian Parker, my husband, for encouraging me to push forward to complete this journey. I could not have finished this program without his complete support. Appreciate goes out to my children, CJ Parker and Clay Parker for their understanding and patience over the past two years. They have done a tremendous job of stepping up and helping out.

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1. INTRODUCTION

1.1. BACKGROUND

Methamphetamine (meth) is a common illegal drug of abuse in the United States that is frequently produced in clandestine "meth labs". These labs have been found in many different types of places such as houses, apartments, hotel and motel rooms, vehicles, rural outbuildings and barns (USEPA 2013). In the year 2012, there were 11,210 clandestine meth lab incidents reported in the United States. Out of those incidents, 1,825 were reported in Missouri as seen in Figure 1.1 (DEA 2013).

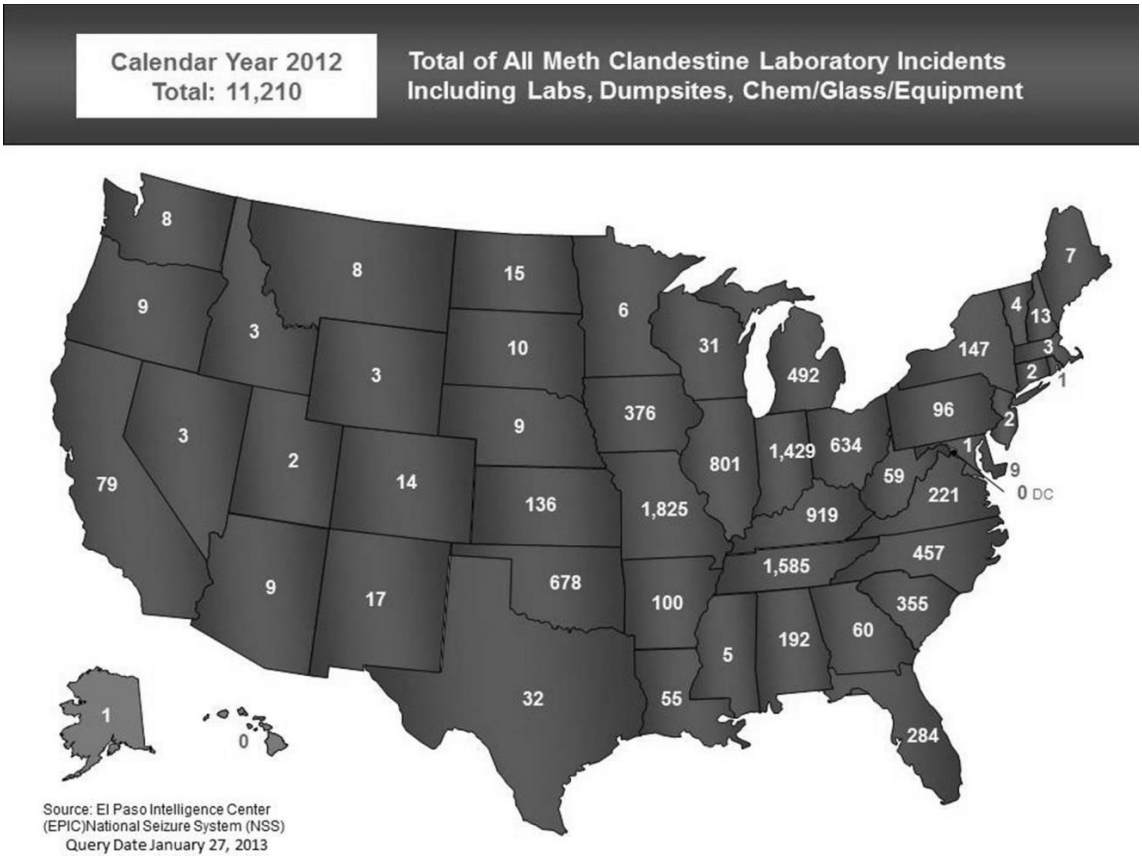


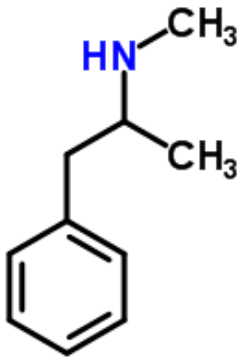
Figure 1.1. Clandestine meth laboratory incidents in the United States in 2012.

Contamination that results from these laboratories can expose future occupants of affected residences to methamphetamine and other chemicals. There are many possible ways that meth in a contaminated building can be taken into the body: inhalation, ingestion of contaminated food, transfer of meth from surfaces to mouth (hand-to-mouth exposure) and absorption through the skin. This research explores how much airborne meth can accumulate in skin oil, helping us better understand human exposure through air-to-skin uptake and object-to-mouth ingestion from objects coated in skin oil.

1.2. PROPERTIES AND HEALTH EFFECTS OF METHAMPHETAMINE

The systematic name for methamphetamine is N-Methyl-1phenyl-2-propanamine and the molecular formula of is $C_{10}H_{15}N$. Table 1.1 identifies the structure and some properties of methamphetamine (Chemspider 2014).

Table 1.1. Structure and properties of methamphetamine

Structure	Properties	
	MW (g/mol)	149.23
	ρ (g/cm^3)	0.907
	Log K_{ow} (Log octanol-water partition coefficient at 25°C)	2.07
	Log K_{oa} (Log octanol-air partition coefficient at 25°C)	6.08

Methamphetamine is a highly addictive drug due to its similarity with dopamine and the fact that 50% of the meth persists in the body unchanged for 12 hours (NIDA 2013). Meth was initially manufactured as a bronchial dilator but was later prescribed to treat medical conditions such as narcolepsy, attention deficit disorder, obesity and fatigue (Hunt et al. 2006).

Exposure to methamphetamine can include a variety of symptoms that include blurred vision, weight loss, light-headedness, chest pain, arrhythmias (irregular heartbeat), hypertension (high blood pressure), hypotension (low blood pressure) and tachycardia (rapid heartbeat) (Salocks 2009). A sub-chronic reference dose (RfD) is a concentration or a dose of a drug in which it is not likely that adverse health effects will occur. For methamphetamine, this dose has been established at $2.7x10^{-4}$ mg/kg-day (Salocks 2009). This dose was based on a lowest observable adverse effect level (LOAEL) of 0.08 mg/kg/day (Chapman 1961).

1.3. ILLICIT PRODUCTION OF METHAMPHETAMINE

Methamphetamine is simple to produce using over-the-counter cold medications that contain ephedrine or pseudoephedrine. There are several different methods for producing illicit meth. The three main methods include the phosphorus, birch and amalgam methods (ADEQ 2008). During a common synthesis process the aqueous free base form of the drug is converted to the methamphetamine hydrochloride (meth-HCl) form by bubbling hydrogen chloride gas through an aqueous solution (Salocks et al. 2014). The meth-HCl contaminates the lab environment as it is released into the air during this phase of the production process which is sometimes referred to as the salting

out stage (Martyny et al. 2007). A large amount of waste and contamination is produced during the synthesis of meth. According to Salocks and Kaley (2003) six or more pounds of hazardous materials or chemicals are produced for every pound of meth that is synthesized.

The meth-HCl has a negligible vapor pressure so it is likely that it will stay where it lands and accumulate on the surfaces. However, when the meth-HCl is in the presence of moisture it can be converted back into its free base form, which has a vapor pressure of 0.147 mmHg at 25°C (Chemspider 2014) and can be transported through the gas phase further into building materials. Over time, the free base meth can be transported back into occupied spaces even after remediation. Poppendieck et al. (2014) showed that painting over methamphetamine, contaminated wallboard does not effectively encapsulate the meth and that elevating temperatures during remediation does not significantly reduce the emissions of the meth from the wallboard. Both of these remediation methods are suggested by the Missouri Department of Health and Senior Services (MDHSS) (MDHSS 2000).

1.4. REMEDIATION OF CLANDESTINE METHAMPHETAMINE LABS

Guidelines for the remediation of clandestine methamphetamine laboratories were established by the United States Environmental Protection Agency (USEPA) (USEPA 2013). According to these guidelines, there are two basic efforts required to remediate a former meth house so that it is safe for reoccupation. These efforts include 1) removing the gross contamination such as containers of chemicals and equipment used to make the drug, and 2) remediating the interior of the structure and the surrounding land, surface

waters and groundwater. It is recommended that the interior structure remediation be accomplished by removing contaminated items such as carpet, furniture, clothes and surfaces with obvious stains. The area should then be aired out with fresh outdoor air. The entire area should be vacuumed using a vacuum with a high efficiency particulate air (HEPA) filter, the dust from the HVAC system should be removed and the filters replaced, and the walls and ceilings should be cleaned with a detergent solution (USEPA 2013).

Final clean-up standards are based on wipe samples to determine the level of surface contamination of methamphetamine. The EPA and most of the states have established voluntary guidelines, which require or recommend that the surface concentration of meth meet a certain standard after remediation. These standards range from 0.05 µg/100cm^2 to 0.5 µg/100cm^2 with the most common standard set at 0.1 µg/100cm^2 (USEPA 2013).

1.5. EXPOSURE AND UPTAKE OF METHAMPHETAMINE

Methamphetamine exposure in contaminated buildings can occur by several routes. Those routes include inhalation, ingestion of contaminated food, hand-to-mouth exposure (transfer from surfaces to the mouth) and absorption through the skin (air-to-skin or surface-to-skin).

One of the less recognized routes of exposure and uptake is absorption through the skin. This route of exposure was studied by Salocks et al. (2012). This study evaluated the effect of pH and volatility on the rate of dermal absorption. The study showed that meth-HCl is sensitive to pH and becomes unstable at pH values greater than

about 4 or 5 at which time it converts back into its free base form. However, the normal surface pH of skin ranges from 4 to 6 (Zheng et al. 2012). Salocks et al. (2012) were able to conclude that under normal skin pH conditions the meth-HCl would infiltrate into and through the skin soon after exposure. Weschler and Nazaroff (2012) examined the dermal uptake and permeation of semi volatile organic compounds (SVOC) though the epidermis and concluded that the internal dose due to dermal uptake and permeation could exceed an inhalation dose for many compounds. Exposure to meth due to dermal uptake can lead to higher doses being delivered directly to tissues and organs via blood because the skin does not have the interceding steps that help reduce the resulting dose (Weschler and Nazaroff 2012).

Object-to-mouth transfer of chemicals can occur by direct mouthing of objects, or by transfer to hand, then to the mouth. Indoor surfaces are often coated with a material that includes skin oil (Weschler and Nazaroff 2008). Therefore, understanding the interactions of methamphetamine with skin oil coatings will be key to understanding how much will accumulate on indoor surfaces.

1.6. SKIN OIL COMPOSITION AND METHAMPHETAMINE ACCUMULATION

Morrison et al. (2014) found that skin oil has a very high, but highly variable capacity for methamphetamine. They reported an average mass normalized partition coefficient of 1200 µg meth/g SO/ppb with results varying from ~500 to 1500 µg meth/g SO/ppb at a relative humidity of 30% after 60 days of exposure to gas phase methamphetamine. At 60% relative humidity, they reported an average coefficient of

1620 µg meth/g SO/ppb with results varying from ~750 to 2900 µg meth/g SO/ppb. It was hypothesized in that study that the wide range of partition coefficients observed was due to the variability in skin surface pH and skin oil composition among individuals. The work suggests that any coated surface will accumulate a large amount of meth that would greatly exceed surface concentration standards even at very low methamphetamine air concentrations.

Skin oil is a complex mixture of compounds including wax esters, triglycerides, fatty acids, cholesterol esters, free cholesterol, squalene and vitamin E (Lu et al. 2009, Stefaniak et al. 2010). The free fatty acids in the skin oil may contribute acidity, which may increase the capacity of the skin oil for methamphetamine. The fatty acid protons may directly associate with the amine group in methamphetamine, which could also increase the capacity for meth interactions.

Skin oil also has an apparent "pH" that is often related to the health of skin, permeability, etc (Hachem et al. 2003). The skin pH may influence the acid-base partitioning of compounds such as methamphetamine. The pKa of methamphetamine is 10.21 (Chemaxon 2013). This means that methamphetamine transitions from its un-ionized "free base" form to its protonated, salt form at a pH of about 10. For a pH below this value, in an aqueous solution, most of the meth would be protonated. This mechanism may help increase the skin oil capacity for methamphetamine by increasing the ability of meth to accept the protons from the fatty acids.

It was hypothesized by Weschler and Nazaroff (2008) that most indoor surfaces are coated with a thin layer of skin oil. In the work presented by Weschler and Nazaroff (2012) it was suggested that the abundance of an SVOC on a surface coated with a thin

film of organic matter could be approximated fairly well by using its chemical and physical properties. For the chemicals discussed in the work, they were able to make predictions of a partition coefficient between the skin-surface lipids and the SVOC in the gas phase but what about real partition coefficients of SVOC's or other chemicals with skin oils. Other questions that arose when reviewing the results of Weschler and Nazaroff (2012) are what if the compound is highly polar, acidic or basic and will the predictions for partitioning into skin-surface lipids be accurate?

1.7. MOTIVATION FOR THIS RESEARCH

The free base meth that is transported back into the occupied space after remediation can accumulate on household furnishings, clothing, toys, exposed skin and surfaces coated with skin oil. By measuring the absorption kinetics and the partition coefficients in real and artificial skin oil compositions, we can better understand the occupant exposure routes.

Previous work has been done to try to predict a partition coefficient for SVOC's into skin-surface lipids (Weschler and Nazaroff 2012) and to try to measure a partition coefficient for methamphetamine into skin oil (Morrison et al. 2014) but several questions arise from the results in both of these studies. Is the predicted partitioning of methamphetamine into skin oil using the method of Weschler and Nazaroff (2012) accurate? Were the results presented by Morrison et al. (2014) variable due to analytical problems or is there a correlation associated with the composition of the skin oil and the partitioning of methamphetamine into the skin oil?

These are some of the questions that need to be answered to help better understand if occupants of a remediated clandestine meth lab are being exposed to levels of methamphetamine that could be greater than recommended standards.

2. GOALS AND OBJECTIVES

The results of a previous study indicated that the composition of skin oil affected the partitioning of methamphetamine into the skin oil. It is the goal of this study to determine what constituents in skin oil affect the uptake of methamphetamine onto skin oil and to what extent. The following objectives were defined to accomplish this goal.

2.1. OBJECTIVE 1

Quantify the equilibrium partition coefficient for artificial skin oil over a range of gas-phase methamphetamine concentrations and demonstrate reproducibility (with a relative standard deviation of 30% or less).

2.2. OBJECTIVE 2

Quantify the equilibrium partition coefficient for artificial skin oil without fatty acids.

2.3. OBJECTIVE 3

Quantify the equilibrium partition coefficient for real skin oil from several volunteers and compare the results with those obtained from artificial skin oil(s).

PAPER

I. METHAMPHETAMINE ABSORPTION BY SKIN OILS: ACCUMULATED MASS, PARTITION COEFFICIENTS AND THE INFLUENCE OF FATTY ACIDS

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1.1 ABSTRACT

Occupants of former methamphetamine laboratories, often residences, may experience increased exposure through the accumulation of the methamphetamine in skin oil. The objectives of this study were to determine equilibrium partition coefficients of vapor-phase methamphetamine with artificial skin oil (ASO), artificial skin oil without fatty acids and real skin oil. A 10 L flow through stainless-steel chamber and in-line filter holders were used to expose skin-oil coated filters to vapor-phase methamphetamine at concentrations ranging from 12 ppb to 159 ppb and samples were analyzed for exposure time periods from 2 hours to 60 days. For a low vapor-phase methamphetamine concentration range of ~12-28 ppb, the equilibrium partition coefficient was 1499 ± 195 µg meth/g SO/ppb. For a high concentration range of 98-159 ppb, the equilibrium partition coefficient was lower, 394 ± 90.6 µg meth/g SO/ppb,

suggesting some saturation of the available absorption capacity. The partition coefficient for artificial skin oil without fatty acids was 33 ± 6 µg meth/g SO/ppb, much lower than any value measured in this study or a previous 60 day study that used real human skin oil in which an average mass normalized partition coefficient of 1410 ± 840 µg meth/g SO/ppb was measured. We believe that the measured coefficients are much greater than the predicted value due to the presence of organic acids in the skin oil, which contribute protons, lower the pH and increase the capacity for basic organic compounds like methamphetamine. The very large absorption capacity suggests that surfaces covered in skin oils would accumulate methamphetamine to levels that exceed recommended surface remediation standards, even for air concentrations in the low part per trillion range.

KEYWORDS

Methamphetamine, skin oil, artificial skin oil, exposure routes, partition

1.2 INTRODUCTION

Methamphetamine (meth) is a common illegal drug of abuse in the United States that is frequently produced in clandestine "meth labs". These labs have been found in many different types of places such as houses, apartments, hotel and motel rooms, vehicles, rural outbuildings and barns (USEPA 2013). Meth is a highly addictive drug due to its similarity with dopamine and the fact that 50% of the meth persists in the body unchanged for 12 hours (NIDA 2013).

Methamphetamine is fairly simple to produce using over-the-counter cold medications that contain ephedrine or pseudoephedrine. Methamphetamine-hydrochloride (meth-HCl) contaminates the spaces used for the lab as it is released into

the air during the phase of production known as the salting out stage (Martyny et al. 2007). The meth-HCl has a negligible vapor pressure so it is likely that it will stay where it lands and accumulate on the surfaces. However, when the meth-HCl is in the presence of moisture it can be converted back into its free base form, which has a vapor pressure of 0.147 mmHg at 25°C (Chemspider 2014) and can be transported through the gas phase to contaminate other surfaces and penetrate deep into building materials. Over time, the meth that has accumulated within building materials can be transported back into occupied spaces long after surfaces have been remediated. Most US states require or recommend a surface concentration of methamphetamine meet a certain standard after remediation. These standards range from 0.05 μg/100cm^2 to 0.5 μg/100cm^2 with the most common standard set at 0.1 μg/100cm^2 (USEPA 2013).

The free base meth that is transported back into the occupied space after remediation can accumulate on household furnishings, clothing, toys, exposed skin and surfaces coated with skin oil. A previous study showed that skin oil has a very high partition coefficient on a mass-normalized basis (Morrison et al. 2014). Therefore, the oils coating human skin could accumulate a very large relative mass of methamphetamine from building air contaminated with gas-phase meth. This, in turn, results in dermal uptake of meth that may be otherwise ignored in traditional exposure assessments that typically focus on ingestion and inhalation alone. Exposure to vapor phase chemicals by dermal uptake can lead to higher doses being delivered directly to tissues and organs via blood because the skin does not have the interceding steps that help reduce the resulting dose (Weschler and Nazaroff 2012). Skin oil that coats surfaces can also act as a

substrate that concentrates methamphetamine on a surface, thereby increasing object-to-mouth exposure for toddlers.

The methamphetamine absorptive capacity of skin oil is parameterized by a partition coefficient and may be strongly influenced by the composition of skin oil. The partition coefficient, K_m, relates the equilibrium concentration in the skin oil to that in the overlying gas phase. A recent study showed that K_m varied substantially (over 2 orders of magnitude) for skin oil from 14 volunteers (Morrison et al. 2014). We hypothesize that K_m is strongly influenced by the composition of the skin oil, especially the concentration of fatty acids. To examine this hypothesis and to verify that the variability in the Morrison et al. (2014) results was not due to analytical problems, the following objectives were defined: 1) Quantify the equilibrium partition coefficient for artificial skin oil over a range of gas-phase methamphetamine concentrations and demonstrate reproducibility (with a relative standard deviation of 30% or less), 2) Quantify the equilibrium partition coefficient for artificial skin oil without fatty acids and 3) Quantify the equilibrium partition coefficient for real skin oil from several volunteers and compare the results with those obtained from artificial skin oil(s).

1.3 MATERIALS AND METHODS

1.3.1 Chemicals, Supplies and Preparation of Samples

1.3.1.1 Chemicals and supplies. Methamphetamine hydrochloride**,** bromofluorobenzene (BFB), squalene, paraffin wax, olive oil, coconut oil, cottonseed oil, oleic acid, steric acid, cholesterol, vitamin E and methyl oleate were purchased from

Sigma Aldrich (Milwaukee, WI). Spermaceti, hexane (pesticide grade) and ethyl acetate (HPLC grade) were purchased from Fisher Scientific (Hanover Park, IL). Cholesteryl Oleate was purchased from Alfa Aesar (Ward Hill, MA). Fluoropore membrane filters (47mm, PTFE) were ordered from Fisher Scientific (Hanover Parker, IL). Solid phase micro extraction fibers (Supelco 65 µm PDMS/DVB, Stableflex, 23 gauge) were obtained from Sigma-Aldrich. Polypropylene (47 mm) in-line filter holders were purchased from Sterlitech Corporation (Kent, WA).

1.3.1.2 Methamphetamine free base preparation. The methamphetamine hydrochloride was converted to free base methamphetamine following the method outlined by Forester (2013). The method involved dissolving the meth-HCl in methanol to get a 25% (w/v) solution. The methamphetamine solution was mixed with 7N sodium hydroxide (NaOH) at a 1:1 ratio. After allowing the solution to sit, an oil layer formed that was assumed to be 100% free base methamphetamine. All analysis was conducted using this free base meth.

1.3.1.3 Artificial skin oil preparation. The composition of an artificial skin oil (ASO) mixture was informed by those described by (Lu et al. 2009) and (Stefaniak et al. 2010). These formulations were originally developed to closely resemble human sebum.

1.3.1.4 Artificial skin oil without fatty acids preparation. A second artificial skin oil was prepared that eliminated the fatty acids (ASO-2). The new target % (w/w) was determined by subtracting the percentage of fatty acids added to the original recipe

and then using the ratio to calculate the percentage required to maintain the same ratios for each constituent group and component. The final composition of both the artificial skin oil and the artificial skin oil without fatty acids can be seen in Table 1. To verify that most of the fatty acids were absent in the ASO-2, an experiment was conducted by coating filters with 99% pure methyl oleate, which was chosen to mimic the triglycerides and other esters in skin oil without contributing protons.

1.3.1.5 Preparation of coated filters. The mass of a clean PTFE filter was first recorded. When preparing samples for the flow through chamber approximately 0.005 g of ASO was applied to the filters using a clean, circular dense-foam sponge making sure to have a thin coating covering the entire surface of the filter. When preparing samples for the filter holder apparatus approximately 0.0015 g of one of the artificial skin oils or methyl oleate was applied to the center of the filter using the small rectangular end of a triangular dense-foam sponge. The mass of the filter with the absorbent was immediately recorded and then placed in either the exposure chamber or a filter holder.

To prepare filters coated with real skin oil volunteers were instructed to wash their face with a face cleansing soap in the morning and not to apply any types of lotions or creams. Before collecting skin oil, the pH of skin was measured at each temple, above each eyebrow and in the center of the forehead using a Mettler Toledo InLab Surface pH probe. A clean filter was weighed and the volunteer was asked to wear nitrile gloves while rubbing one filter on the center of the forehead and a second filter on each temple. The filter was immediately weighed again and then placed inside an in-line filter holder.

1.3.2 Exposure Systems. Two different systems were used to expose the coated filters to vapor phase methamphetamine. The first system was a 10 L flow through chamber that is identical to that used by Morrison et al. (2014) and exhibits mass-transfer conditions similar to indoor environments. The time to reach equilibrium using this system was approximately 60 days. To generate more rapid results an in-line filter holder system was also designed that allowed for an equilibration time of 5-15 days.

1.3.2.1 10L flow through chamber. Experiments were conducted using a 10L flow-through, electro polished stainless steel chamber as seen in Figure 1. The filters were placed on a three-tier perforated stainless steel rack. A methamphetamine diffusion vial was kept in a temperature-controlled bottle at 35°C and meth was evaporated into a stream of air that was humidified to approximately 60% RH at 25°C. The total flow rate for the gas stream was 2 L/min with the methamphetamine concentration at about 28 ppb. The entire system was housed in a temperature-controlled cabinet at 25°C. The concentration of the methamphetamine was measured as described in section 1.3.4.

1.3.2.2 Filter holder apparatus. An in-line filter holder exposure apparatus shown in Figure 2 was designed to decrease the amount of time needed to reach equilibrium. The temperature of the methamphetamine diffusion vial was set at 30°C and the concentration of the methamphetamine in the gas stream ranged from ~12 to 159 ppb. The humidity of the gas stream was maintained at ~60% at 25°C and the total flow was kept at 2 L/min. The entire system was housed in a temperature-controlled cabinet at 25°C.

1.3.3 Experimental Procedures

1.3.3.1 Flow through chamber. Artificial skin oil coated filters were placed inside the chamber to be exposed to methamphetamine vapor at a concentration ranging from ~19 to 22 ppb for anywhere from 2 hours to 60 days. Duplicate samples were exposed for each time frame (2, 4, 6, 12, 24 and 48 hours and 3, 4, 5, 6, 10, 20, 30 and 60 days) and then analyzed as described in section 3.4.5. The flow through the system was monitored regularly throughout each experiment.

1.3.3.2 In-line filter holders. A filter coated with ASO, ASO-2, methyl oleate or real skin oil was placed inside a filter holder and then placed in-line with the methamphetamine gas stream at a concentration ranging from ~12 - 159 ppb. The coated filters were exposed from 1 to 15 days, and then removed and extracted for analysis following the procedure described in section 1.3.5. All filters were exposed to the vapor phase methamphetamine for 5 days once it was determined that the partition coefficient was not increasing after 5 days of exposure for the high methamphetamine concentration experiments. Duplicate samples were exposed for each sample type. Flow through each filter holder and through the system was monitored regularly throughout each experiment.

1.3.4 Gas Stream Sampling and Analysis. The methamphetamine in the flowing gas stream was determined gravimetrically. The diffusion vial was weighed biweekly and the concentration was calculated as the difference in mass divided by the

cumulative volumetric flow through the system over the time interval. This gas stream was used to perform a 5 point calibration curve of the SPME fiber. The calibration points included 1, 3, 5, 7 and 9 minute samples.

SPME samples were obtained by inserting the SPME fiber into the meth gas stream for 5 minutes. All SPME samples were analyzed immediately after collection utilizing an Agilent gas chromatograph with mass spectrometry detection (GC/MS) using manual injections and the following operating conditions:

Inlet:	Temperature - 260°C
	Constant Pressure – 6.37 psi
	Split Ratio – 10:1
Carrier Gas:	Helium
Column:	HP-5MS (5% Phenyl Methyl Siloxane – 0.25 mm x 30 m x 0.25 µm)
Oven:	Initial temperature 100°C with a ramp of 20°C/min to a final temperature of 280°C for a total run time of 9 minutes
Detector:	MS – Transfer line at 280°C, Quad at 150°C, Source at 230°C in scan mode (40-180 amu)

1.3.5 Filter Extraction and Analysis. Immediately upon being removed from the exposure apparatus, the filters were placed into a 7.5 mL vial. The samples were extracted by adding 5.0 mL of a 1% ethyl acetate in hexane solution to the vial. The vial was sonicated for 10 minutes before the extract was filtered through a nylon 0.2 µm syringe filter into a separate 7.5 mL vial. BFB prepared at 1,000 ppm in ethyl acetate

was utilized as an internal standard. A 1.0 mL aliquot of the sample extract was transferred to a 2.0 mL GC vial and spiked with 10 µL of the BFB internal standard. Each sample was analyzed immediately after sample extraction utilizing an Agilent GC/MS using the following operating conditions:

Inlet:	Injection volume – 1.0 µL Temperature - 250°C Constant Pressure – 3.94 psi Split Ratio – 40:1
Carrier Gas:	Helium
Column:	HP-5MS (5% Phenyl Methyl Siloxane – 0.25 mm x 30 m x 0.25 µm)
Oven:	Initial temperature of 50°C – hold for 4 minutes and then ramp at a rate of 20°C/min to a final temperature of 250°C for a total run time of 14 minutes
Detector:	MS – Transfer line at 280°C, Quad at 150°C, Source at 230°C in single ion mode (m/z = 58, 91, 95, 175)

A seven point calibration curve was performed that included 0.5, 1.0, 2.5, 5.0, 10, 20 and 25 µg/mL meth standards in a 1% ethyl acetate in hexane solution. Each standard was spiked with BFB and then analyzed. The ratio of the meth peak area to the BFB peak area versus the meth concentration yielded a linear response and the equation of that line was used to calculate the concentrations of the methamphetamine extracted from the samples. A calibration check was analyzed with each batch of samples to verify that the

calibration was still valid. A method detection limit (MDL) of 0.08 µg/mL was determined and a limit of quantitation (LOQ) was established at 0.30 µg/mL. These values were determined following the procedures outlined in 40 CFR Part 136, Appendix B, Revision 1.11 (2011).

1.3.6 Calculations. The mass-normalized accumulation, A_m, was determined as follows,

$$\frac{m_{meth}}{m_{SO}} = A_m \qquad (1)$$

where m_{meth} (µg) is the mass of meth accumulated and m_{so} (g) is the mass of methamphetamine-free skin oil coating.

The mass-normalized partition coefficient, K_m, was determined as follows,

$$\frac{m_{meth}}{m_{SO} * C_{meth}} = K_m \qquad (2)$$

where c_{meth} (ppb) is the mixing ratio of the freebase meth in the chamber air at the time the samples were exposed.

The area-normalized partition coefficient, K_a, was determined as follows to compare against remediation standards,

$$\frac{m_{meth}}{A_{filter} * C_{meth}} = K_a \qquad (3)$$

where A_{filter} (cm^2) is the cross-sectional area of the filter.

1.4 RESULTS AND DISCUSSION

1.4.1 Range of Partition Coefficients. The overall results from this study are shown in Table 2. The methamphetamine concentration at the lower range includes results for data from both the 10 L exposure chamber experiments and the in-line filter holder experiments. The higher meth concentration range includes data from the in-line filter holder experiments only. When the methamphetamine concentration was at the lower range of 12 to 28 ppb the average K_m determined was 1499 ± 195 µg Meth/g ASO/ppb but at the higher methamphetamine concentration range of 98 to 159 ppb the average K_m found was 394 ± 96 µg Meth/g ASO/ppb. Filters coated with artificial skin oil without fatty acids yielded a much lower K_m of 33 ± 6 µg Meth/g ASO/ppb. Methyl oleate coated filters yielded a very similar K_m of 35 ± 2 µg Meth/g ASO/ppb. Both the ASO-2 and the methyl oleate results were obtained from the in-line filter holder experiments with a methamphetamine concentration range of 98 to 118 ppb. An average K_a value of 51 ± 8.4 µg meth/100 cm^2/ppb was calculated using data from the flow through chamber at the lower meth concentration range.

The results for real skin oil exposed to vapor phase methamphetamine using the in-line filter holder apparatus are given in Table 3. A wide range of variability between both the volunteer and the location on the face that the samples were taken from can be seen in these results. The results from this study are very similar to the results seen in the previous study by (Morrison et al. 2014) in that they are very variable among the volunteers.

1.4.2 Reproducibility of ASO and Variability of RSO. The results from the artificial skin oil experiments are reasonably reproducible for a narrow range of gas-phase methamphetamine concentrations. For example, the average K_m is 459 ± 80.1 µg meth/g SO/ppb for four of the experiments conducted using the in-line filter holders and a methamphetamine concentration ranging between 98 to 112 ppb. This partition coefficient is different from the results given in Table 2 because those results include a fifth experiment that was conducted at a meth concentration of 159 ppb. The data from that experiment is being excluded here to demonstrate reproducibility for narrow ranges of gas concentrations. Similarly, the average K_m was 1499 ± 195 µg Meth/g SO/ppb from experiments conducted in the 10 L flow through system and the in-line filter holder system with the methamphetamine concentration ranging between 12 to 28 ppb. The relative standard deviation for experiments performed at a narrow range of concentrations is typically less than 25%.

The K_m for the real skin oil experiments yielded notably different results for each volunteer and between the locations that the sample was obtained from on the individual as shown in Table 3. The samples acquired from above the eyebrows and the center of the forehead yielded overall higher K_m values (327, 385 and 1095 µg meth/g RSO/ppb) than the samples attained from the temples (65.1, 230 and 789 µg meth/g RSO/ppb) for each of the individuals. It was also noticed that the K_m for the forehead samples and for the temple samples differed significantly between each of the volunteers. Other noteworthy finding are that there seems to be no correlation between the K_m values and the pH of the different sample locations, and that the K_m values obtained for real skin oil are greater than the K_m values seen in the RSO-2 and methyl oleate experiments. The

composition of skin oil between individuals and among different locations on a single person differs significantly, which could explain the variability seen in these results.

1.4.3 Effects of Fatty Acids. Experiments were conducted to determine if the composition of skin oil affected the equilibrium accumulation or partition coefficient of methamphetamine. At approximately 100 ppb, an average partition coefficient of 459 ± 80.1 µg Meth/g SO/ppb was observed for ASO coated filters. For ASO without fatty acids the average K_m was 33 ± 6 µg Meth/g ASO/ppb. The average K_m obtained when using methyl oleate was 35 ± 2 µg Meth/g ASO/ppb. Therefore, fatty acids are responsible for most of the observed methamphetamine accumulation in artificial skin oil. These results support the hypothesis that the variability observed in the experiments using real skin oil (in this research and in (Morrison et al. 2014)) are due to the variable composition of skin oil, specifically the fatty acid content.

1.4.4 Influence of the Gas Phase Methamphetamine Concentration. Results from this study, indicate that the partitioning of meth into skin oil is dependent on the gas phase concentration of the methamphetamine, but does not exhibit linear partitioning over the concentration range studied. In Figure 3 are shown equilibrium accumulation results, A_m, for a gas phase meth concentration range from 12 to 159 ppb. Meth accumulation rises with concentration at the lower end, but appears to saturate at a concentration of about 100 ppb or higher.

These results may be further evidence that the fatty acid content affects the absorption capacity of the skin oil. This behavior can be compared, qualitatively, to a

Langmuir isotherm. For example, the skin oil has a limited number of sites that the meth can interact with (fatty acid protons). At low meth concentrations, there are plenty of sites, and partitioning appears to be linear. When the meth concentration is higher, the available sites are running out and the skin oil capacity begins to "max out".

Figure 4 shows how the partition coefficients (µg meth/g ASO/ppb) decrease as the concentration rises. This is a direct result of saturation observed in Figure 3, i.e. a constant accumulation value divided by an increasing concentration value. If the absorption isotherm were linear then the data in Figure 4 would be a straight horizontal line instead of decreasing with increased meth concentration.

1.4.5 Approach to Equilibrium

1.4.5.1 Flow through chamber. Two partition coefficients are reported for the flow through chamber data. After 60 days a K_m value of 1600 ± 270 µg meth/g ASO/ppb was observed while a K_a value of 51 ± 8.4 µg meth/100cm^2/ppb was identified. The mass of meth accumulating on the artificial skin oil may still have been rising at day 60 (not quite at equilibrium) as shown in Figure 5. However, a mass-transfer analysis by Morrison et al. (2014) showed that it is probable that, even though K_m appears to be rising, the system was very near equilibrium. Therefore, these values are close to the partition coefficient or represent a lower bound for the partition coefficient at 25°C with the methamphetamine vapor concentration ranging from ~19 to 22 ppb.

1.4.5.2 In-line filter holders. The initial filter holder experiment results using the in-line filter holders produced a K_m of 1109 ± 514 µg Meth/g SO/ppb at 5 days and 1745 µg Meth/g SO/ppb at 15 days with the methamphetamine vapor concentration at approximately 10 ppb. Based on results shown in Figure 6 we anticipate that equilibrium is being approached at 15 days of exposure. At a higher concentration (98-159 ppb), equilibrium was achieved more rapidly (about 5 days) (shown in Figure 7), possibly because the partition coefficient is much smaller at 459 ± 80.1 µg Meth/g SO/ppb. At this higher concentration, filters were exposed for 5 days to achieve equilibrium when using the in-line filter holder apparatus.

1.4.6 Discussion

1.4.6.1 Fatty acid composition and comparison with saturation methamphetamine concentration. The presence of fatty acids in skin oil significantly increases its methamphetamine capacity, but also results in non-linear absorption. This was demonstrated when the artificial skin oil without fatty acids and the methyl oleate was exposed to the vapor phase meth and resulted in an average K_m for both coatings that was more than 11 times lower than the average value of the K_m for the experiments conducted with ASO. The theoretical mass normalized partition coefficient based on the procedure outlined by (Weschler and Nazaroff 2012) is 8.1 µg meth/g SO/ppb. This is much lower than any value measured in this study or a previous 60-day study that used human skin oil in which an average K_m of 1200 ± 570 µg meth/g RSO/ppb was measured (Morrison et al. 2014). As shown throughout this paper the

composition of skin oil, most notably the fatty acid content, influences how much meth will interact. It is believed that this effect is due to the affinity of the amine group in meth for the protons on the fatty acids. If this is the case then it is anticipated that each individual's exposure to meth will vary significantly depending on the composition of his or her skin oil because the composition of the skin oil is going to significantly affect the absorption and partition coefficient for each person.

If fatty acid groups and their associated protons are responsible for enhanced methamphetamine absorption then a theoretical maximum accumulation of methamphetamine ($A_{m,max}$) may be estimated. Assuming that one amine from the meth can associate with one available proton from the fatty acids and that all fatty acid protons are available for reaction then a maximum methamphetamine accumulation value can be calculated as follows:

$$A_{m.max} = \frac{m_{meth}}{m_{ASO}} = wt\%FA\left(\frac{MW_{meth}}{MW_{FA}}\right)\left(\frac{10^6 \mu g}{g}\right) \qquad (4)$$

where *wt%FA* is the weight % of fatty acids in ASO (27.6%), MW_{meth} is the molecular weight of methamphetamine (149 g/mol) and MW_{FA} is the mean molecular weight of fatty acids (283 g/mol)

$$K_m = \frac{A_{m,max}}{C_{meth}} \qquad (5)$$

Equation 5 shows how the apparent partition coefficient, K_m, would decrease as the air concentration increases if saturation is reached, which is what was observed throughout the study.

The $A_{m,max}$ to the ASO in this study is estimated to be 145,000 µg meth/g ASO. This value is within a factor of ~2 of the highest accumulation value observed in this study, suggesting that proton-amine interactions are strongly influencing the absorptive capacity. Since most values measured in this study are lower than the maximum estimated value, not all fatty acid protons are readily available for interacting with the meth.

1.4.6.2 Comparison of results against health based remediation standards.

The K_a determined in the initial chamber experiments indicates that ~50 µg of meth can accumulate in a 100 cm^2 area if the equilibrium vapor phase methamphetamine concentration is just 1 ppb. When compared to the recommended remediation standard of 0.1 µg Meth/100cm^2, ASO coated filters exceed this standard by ~500. Alternatively, air concentrations would have to be 0.002 ppb or lower for skin-oil coated surfaces to meet the standard. Both partition coefficients found in the chamber experiments are anticipated to be lower on skin than those measured in the chamber because the average skin surface is at a higher temperature (32°C). Also, $K_{,a}$ for human skin would be somewhat lower still since the experiments conducted in this study used an artificial skin oil thickness of about 3 µm while (Weschler and Nazaroff 2012) report an average skin-surface lipid thickness of ~1 µm. Even with a lower partition coefficient and a thinner skin-oil film, equilibrium with skin surfaces may not be achievable due to the continuous

production of skin oil, periodic washing off of skin-oils and transport through the skin. However, it is hypothesized by (Weschler and Nazaroff 2008) that skin oil coats much of the available indoor surface areas. The surfaces could be at lower temperatures than what we tested thereby possibly increasing the K_m for surfaces coated with skin oil. However, the results in this study and the results from Morrison et al. (2014) suggest that the highly variable composition of real skin oil will influence absorptive capacity to a much greater degree than will the relatively narrow range of indoor surface temperatures.

1.5 CONCLUSIONS

After a clandestine methamphetamine lab has been remediated and released for re-occupancy, it is possible that meth can still be released from the building materials back into the occupied space. It is our belief that sustained air concentrations of meth that are much less than 1ppb can pose health risks to the new occupants due to a much higher possibility of exposure through the accumulation of meth from the air to skin oil than what has traditionally been considered. We recommend that air concentrations of meth along with surface concentrations be measured periodically after remediation to ensure that the remediation was effective.

The results in this study are for methamphetamine accumulation on artificial skin oil however, the results suggest that other chemicals may also be of concern. When modelling the partitioning of semi-volatile organic compounds onto skin oil, the composition, temperature, moisture content and pH should all be taken into account.

Future studies should include examining the effects that temperature and relative humidity have on the uptake of methamphetamine to skin oil, and altering the artificial

skin oil in other ways to determine what other components of skin oil could be attributing to the uptake of meth such as the triglycerides. The study should also be expanded to include other semi-volatile organic compounds.

1.6 ACKNOWLEDGEMENTS

We would like to thank Dr. Honglan Shi for developing analytical methods for methamphetamine extraction and quantification, and the ERC for the use of the instruments. We would also like to thank Melissa Buechlein, Hongwan Li and Brandon Pollpeter for their assistance.

1.7 SUPPLEMENTARY INFORMATION

Table 1. Composition of artificial skin oils

Constituent	Component	ASO[a]		ASO-2[b]	
		Target Constituent Group % w/w	**Target Component % w/w**	**Target Constituent Group % w/w**	**Target Component % w/w**
Squalene	Squalene	10.6	10.6	14.6	14.6
Wax Esters	Paraffin Wax	25	10	34.5	13.8
	Spermaceti		15		20.7
Triglycerides	Olive Oil	31	7	42.8	9.7
	Coconut Oil		7		9.7
	Cottonseed Oil		17		23.4
Fatty Acids	Oleic Acid	27.6	13.8	NA	
	Steric Acid		13.8		
Free Cholesterol	Cholesterol	3.9	3.9	5.4	5.4
Cholesterol Esters	Cholesterol Oleate	1.9	1.9	2.6	2.6
Vitamin E	Vitamin E	Trace	Trace	Trace	Trace

a – artificial skin oil
b – artificial skin oil without fatty acids

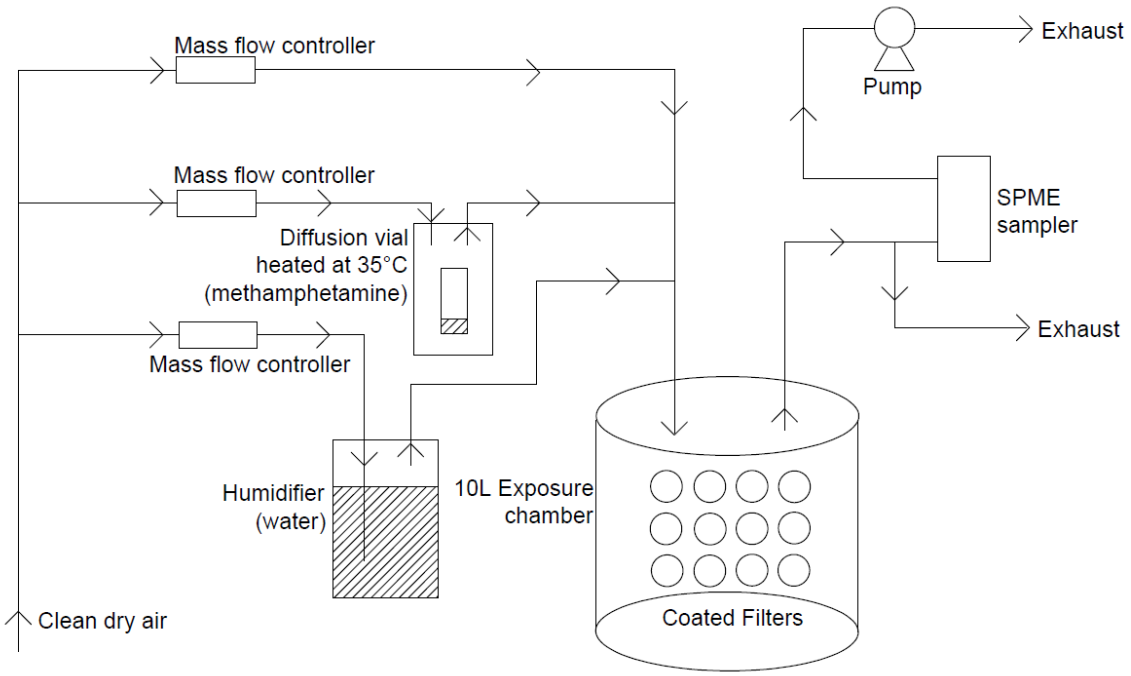

Figure 1. 10 L flow through exposure apparatus used to expose substrates to methamphetamine vapor.

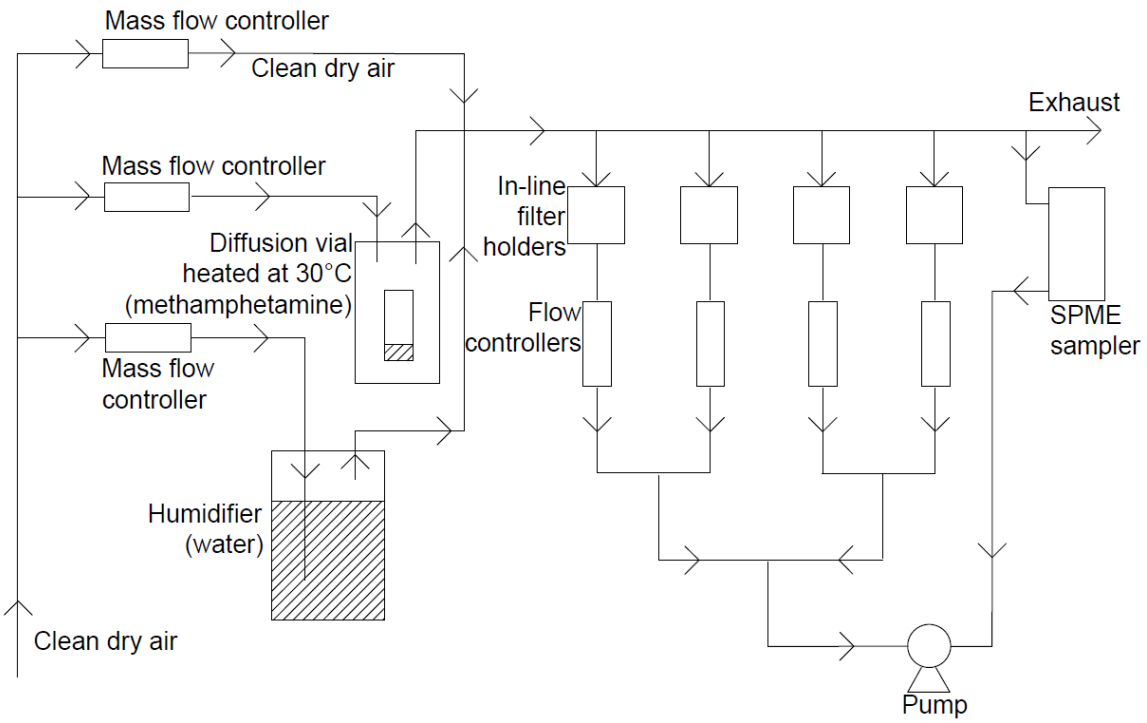

Figure 2. In-line filter holder exposure apparatus used to expose substrates to methamphetamine vapor.

Table 2. Overall results of the artificial skin oil and methyl oleate experiments.

Coating	Meth Conc Range (ppb)	A_m (μg Meth / g ASO)		K_m (μg Meth / g ASO / ppb)	
		Average	Standard Deviation	Average	Standard Deviation
ASO	12 to 28	19621	13183	1499	195
	98 to 159	45521	4521	394	96
ASO-2	98 to 118	3365	606	33	6
MO	118	3929	229	35	2

A_m – Accumulation of methamphetamine per gram of methamphetamine-free coating
K_m – Mass normalized partition coefficient

Table 3. Results of real skin oil exposed to vapor phase methamphetamine.

Coating	Sample ID	pH		A_m (μg meth/g ASO)	K_m (μg meth/g ASO/ppb)
RSO (Forehead)	1	Forehead	5.18	40435	385
		Left Eyebrow	5.37		
		Right Eyebrow	5.35		
	2	Forehead	5.15	116102	1095
		Left Eyebrow	5.10		
		Right Eyebrow	5.29		
	3	Forehead	6.03	34712	327
		Left Eyebrow	6.03		
		Right Eyebrow	5.82		
RSO (Temple)	1	Left Temple	5.31	6838	65.1
		Right Temple	5.24		
	2	Left Temple	5.43	83591	789
		Right Temple	5.29		
	3	Left Temple	6.02	24370	230
		Right Temple	5.99		

A_m – Accumulation of methamphetamine per gram of methamphetamine-free coating
K_m – Mass normalized partition coefficient

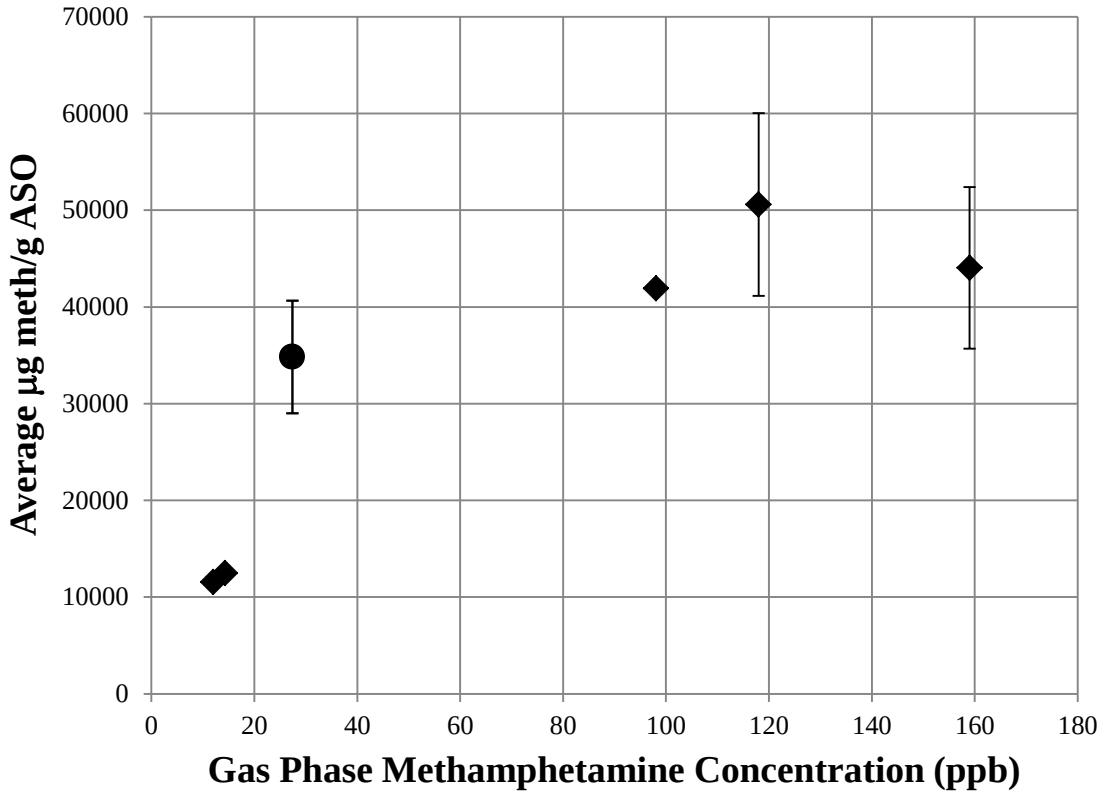

Figure 3. Average methamphetamine accumulation versus the gas phase methamphetamine concentration.

The diamonds represent the data obtained from the in-line filter holder experiments where the circle represents the data obtained in the flow through chamber experiments.

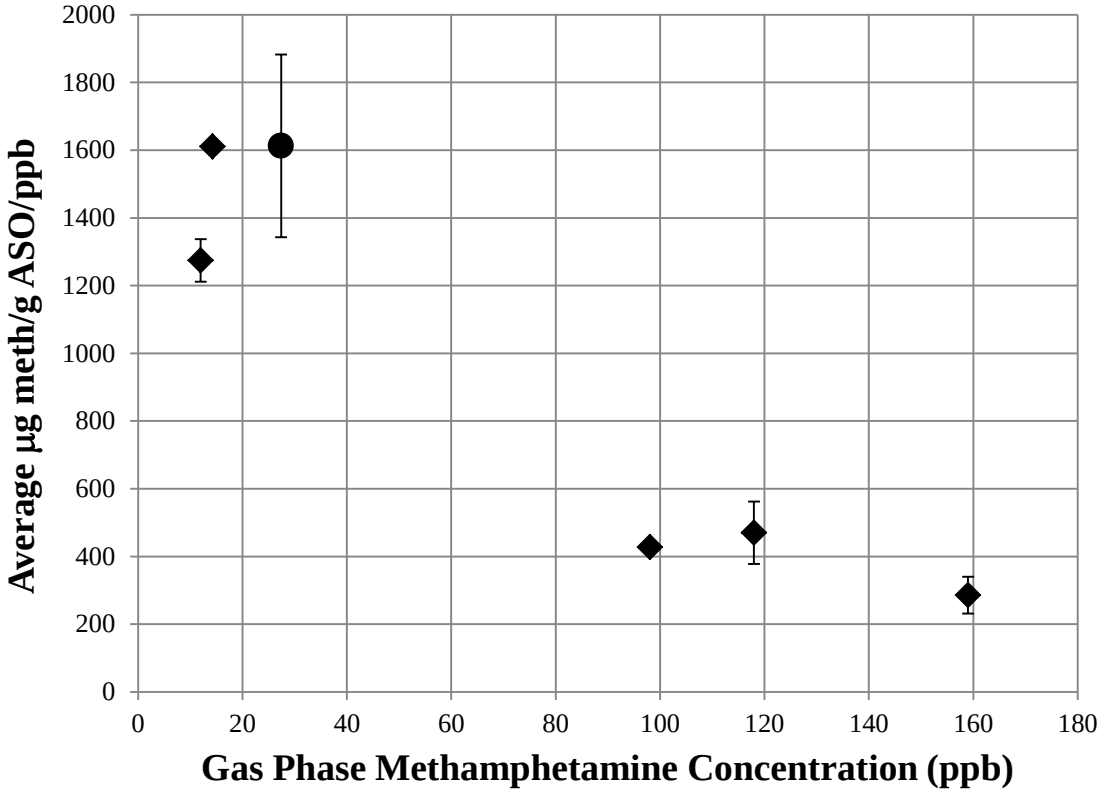

Figure 4. Average K_m versus the gas phase methamphetamine concentration.

The diamonds represent the data obtained from the in-line filter holder experiments where the circle represents the data obtained in the flow through chamber experiments.

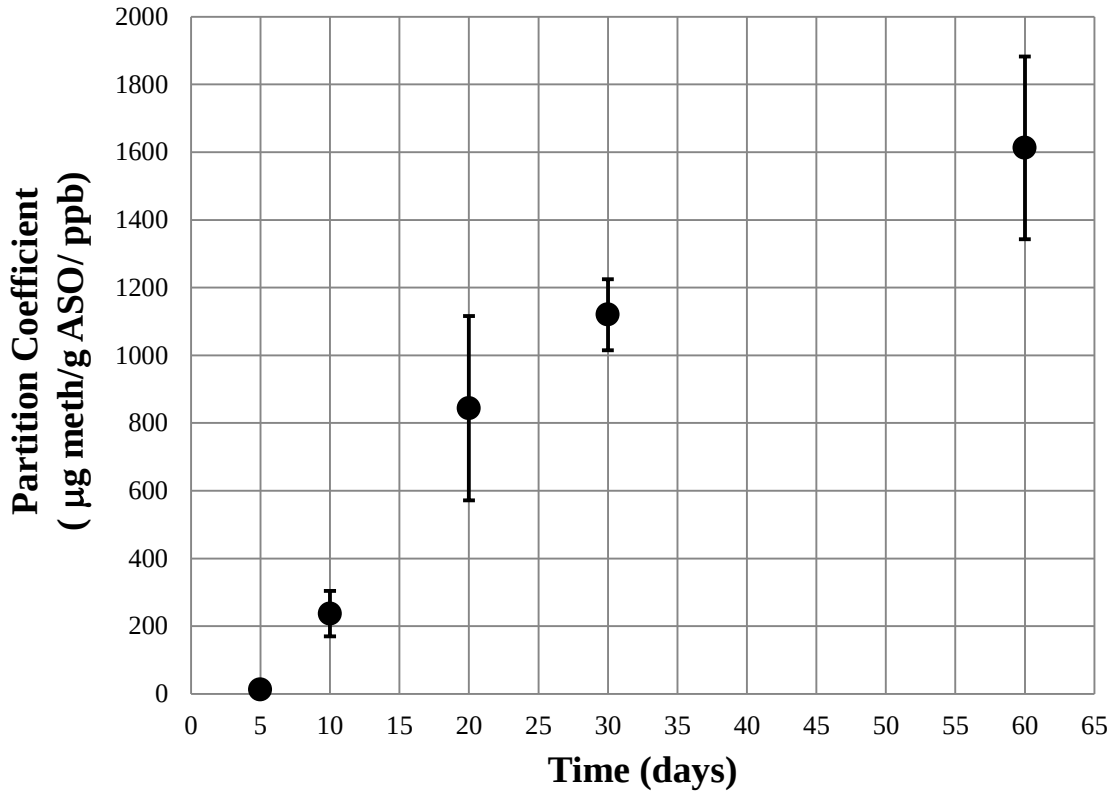

Figure 5. Average K_m versus time.

This graph is indicating that the methamphetamine accumulation on the skin oil may not have reached equilibrium at day 60.

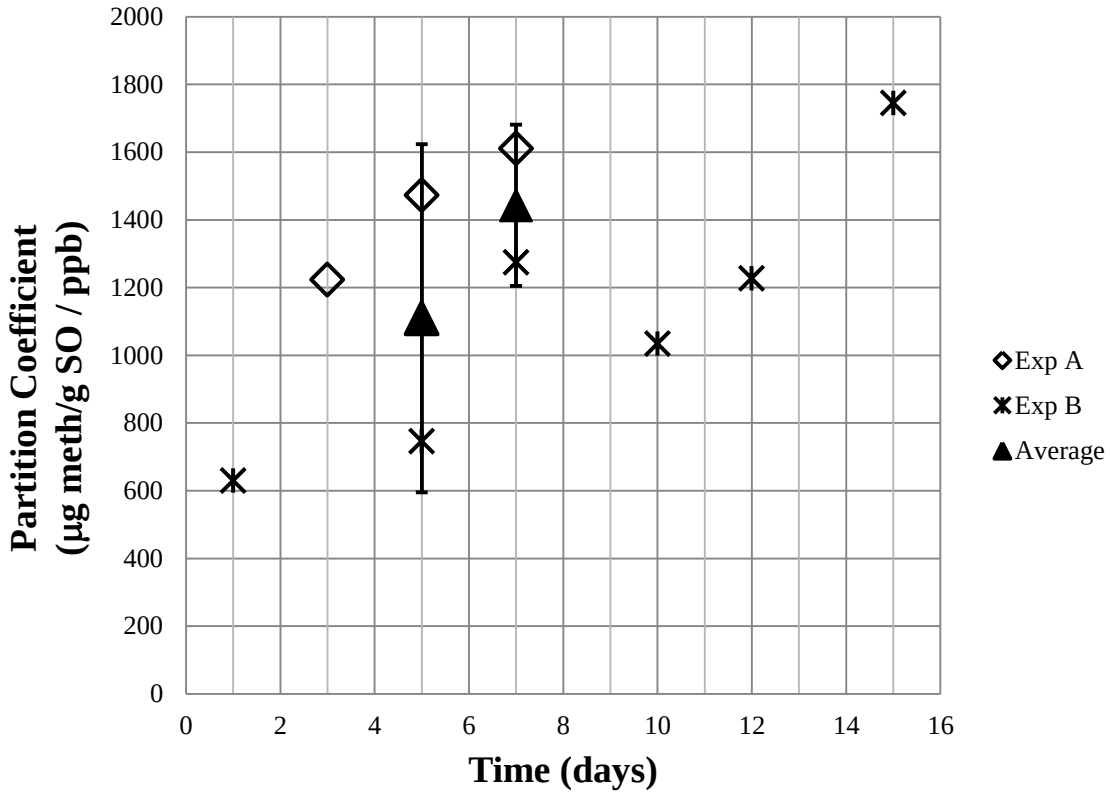

Figure 6. Results for the initial filter holder experiments with a vapor-phase methamphetamine concentration of ~10ppb.

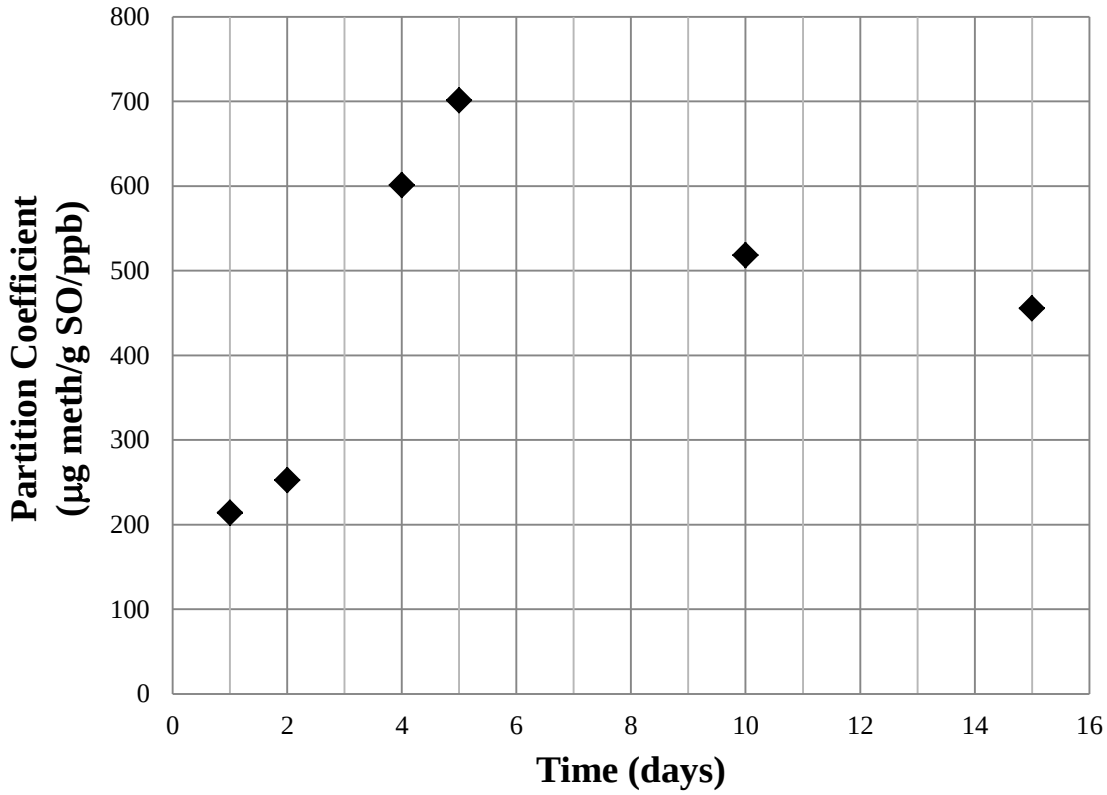

Figure 7. Filter holder partition coefficients using a vapor phase methamphetamine concentration of ~100 ppb.

SECTION

3. CONCLUSIONS

The primary results of this work are presented in the manuscript for publication in Atmospheric Environment. Tables A1, A2, A3and A4 in the Appendix show the results for each experiment conducted. The major findings are reported here as they relate to the objectives outlined in section 2 of this thesis.

Objective 1 was to develop artificial skin oil so that experiments could be conducted to ascertain if the exposure method could be reproduced and determine an average equilibrium partition coefficient for vapor-phase meth with the artificial skin oil. This objective was met. The average K_m using artificial skin oil was determined to be 1499 ± 195 µg meth/g ASO/ppb when the gas phase meth concentration was ~10 ppb. This value is from experiments using the flow through chamber and the in-line filter holder apparatus exposing six different samples. When the gas phase meth concentration was ~100ppb, K_m was determined to be 459 ± 80.1 µg meth/g ASO/ppb by averaging the results from eight samples. These values show that the exposure methods used are reproducible and that the partition coefficient is dependent on the meth concentration in the gas phase.

Objective 2 was to develop artificial skin oil without fatty acids and determine an average equilibrium partition coefficient for vapor-phase meth with this artificial skin oil. This objective was met. The average K_m value obtained when using artificial skin oil without fatty acids was 33 ± 6 µg meth/g ASO-2/ppb. A K_m value for methyl oleate was also determined to verify that most of the fatty acids had been removed from the artificial

skin oil. The value obtained was 35 ± 2 µg meth/g ASO/ppb. These results are further evidence that the methods used in this study are reproducible. The results also demonstrate that the composition of skin oil, specifically the fatty acid content, effect the interactions of methamphetamine with the skin oil.

Objective 3 was to determine an average equilibrium partition coefficient of vapor-phase meth to real skin oil from several different volunteers and compare the results to the partition coefficients for the artificial skin oil and the artificial skin oil without fatty acids. This objective was met. The average K_m for real skin oil samples collected from the forehead was 602 ± 428 µg meth/g RSO/ppb and for samples collected from the temples, the average K_m observed was 361 ± 379 µg meth/g RSO/ppb with a meth concentration of ~105 ppb. The results varied significantly among individuals and between different areas of the face. When compared to the results obtained in the experiments using ASO it is clear to see that these results are extremely variable but still within the same approximate range. It is also noticed that the results are significantly greater for both the K_m observed from the forehead and the temples, than for the artificial skin oil without fatty acids and methyl oleate K_m.

4. PRACTICAL IMPLICATIONS

After a clandestine methamphetamine lab has been remediated and released for re-occupancy, it is possible that meth can still be released from the building materials back into the occupied space. It is our belief that sustained air concentrations of meth that are much less than 1ppb can pose health risks to the new occupants due to a much higher possibility of exposure through the accumulation of meth from the air to skin oil than what has traditionally been considered. We recommend that air concentrations of meth along with surface concentrations be measured periodically after remediation to ensure that the remediation was effective.

The results in this study are for methamphetamine accumulation on artificial skin oil however, the results suggest that other chemicals may also be of concern. When modelling the partitioning of polar, acidic or basic organic compounds into skin oil, chemical properties such as pH should be taken into account.

5. FUTURE RESEARCH

In this work, the partition coefficients of artificial skin oil, artificial skin oil without fatty acids and real skin oil were determined using a temperature of 25°C and a relative humidity of ~60%. The experiments conducted in this study should be repeated at a temperature about 32°C which is the average typical temperature of skin (Weschler and Nazaroff 2012) and at a relative humidity of ~40%, since 60% is the upper part of the comfortable range for human comfort with 30% being the lower end of the range according to (ASHRAE 2013).

To determine what other components of skin oil affect the interactions of meth with skin oil the artificial skin oil should be modified in other ways such as removing the triglycerides which also contain a small fraction of fatty acids. The moisture content of the artificial skin oil should also be modified to determine the effects that moisture has on the uptake of methamphetamine to skin oil. It is our belief that under conditions of higher moisture content there will be more interactions between the meth and the skin oil.

The partitioning of other similar organic compounds to skin oil under different conditions should also be evaluated. We found in this study that the exposure potential to methamphetamine is much greater than expected when looking at the theoretical partition coefficient based on the octanol-air coefficients. This may be the case for other acidic or basic organic compounds as well.

APPENDIX

Table A1. Flow through chamber experiment data.

Coating	Exp Time (days)	Meth Conc (ppb)	A_m (μg Meth / g ASO)			K_m (μg Meth / g ASO / ppb)		
			Sample Result	Avg	Std Dev	Sample Result	Avg	Std Dev
ASO	5.0	27.4	223	275	74	10	12	3
ASO	5.0	27.4	327			15		
ASO	10	27.4	5401	4502	1272	284	237	67
ASO	10	27.4	3602			190		
ASO	20	27.4	12571	16282	5248	651	844	272
ASO	20	27.4	19993			1036		
ASO	30	27.4	20502	21954	2054	1046	1120	105
ASO	30	27.4	23407			1194		
ASO	60	27.4	38953	34834	5825	1803	1613	270
ASO	60	27.4	30715			1422		

Table A2. In-line filter holder experiment data.

Coating	Exp Time (days)	Meth Conc (ppb)	A_m (μg Meth / g ASO)			K_m (μg Meth / g ASO / ppb)		
			Sample Result	Avg	Std Dev	Sample Result	Avg	Std Dev
ASO	7	12.0	11963	11559	571	1319	1274	63
ASO	7	12.0	11155			1230		
ASO	15	12.0	19022	NA		1745	NA	
ASO	3	14.3	9304	NA		1223	NA	
ASO	5	14.3	11300	NA		1473	NA	
ASO	7	14.3	12470	NA		1611	NA	
ASO	5	98.1	41853	41932	112	427	427	1
ASO	5	98.1	42011			428		
ASO	5	118	41161	50598	9440	388	470	92
ASO	5	118	39213			370		
ASO	5	118	49283			438		
ASO	5	118	53204			473		
ASO	5	118	64081			610		
ASO	5	118	56648			540		
ASO	1	159	27676	33405	8101	177	214	52
ASO	1	159	39133			251		
ASO	2	159	40967	38912	2906	266	253	19
ASO	2	159	36857			239		
ASO	5	159	38125	44032	8354	248	286	54
ASO	5	159	49940			324		

Table A3. Data from in-line filter holder experiments using ASO-2 or methyl oleate

Coating	Exp Time (days)	Meth Conc (ppb)	A_m (μg Meth / g ASO)			K_m (μg Meth / g ASO / ppb)		
			Sample Result	Avg	Std Dev	Sample Result	Avg	Std Dev
ASO-2	5	98.1	3751	3365	606	38.2	33	6
ASO-2	5	98.1	3670			37.4		
ASO-2	5	98.1	2824			28.8		
ASO-2	5	98.1	2389			24.3		
ASO-2	5	118	3852			36.3		
ASO-2	5	118	3702			34.9		
ASO-2	15	127	5258	5399	199	41.4	43	2
ASO-2	15	127	5540			43.6		
MO	5	118	3768	3929	229	33.5	35	2
MO	5	118	4091			36.4		

Table A4. Data from in-line filter holder experiments using real skin oil from volunteers

Loc	Coating	Exp Time (days)	Meth Conc (ppb)	A_m (μg Meth / g ASO)			K_m (μg Meth / g ASO / ppb)		
				Sample Result	Avg	Std Dev	Sample Result	Avg	Std Dev
1	RSO-1	5	105	40435	63750	45429	385	602	428
	RSO-2	5	106	116102			1095		
	RSO-3	5	106	34712			327		
2	RSO-1	5	105	6838	38266	40219	65.1	361	379
	RSO-1	5	106	83591			789		
	RSO-1	5	106	24370			230		

Loc 1 – Center of the forehead

Loc 2 – Both sides of the forehead at the temple

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