EVALUATING THE IMPACT OF AMBIENT BENZENE VAPOR CONCENTRATIONS ON PRODUCT WATER FROM CONDENSATION WATER FROM AIR TECHNOLOGY

by

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ABSTRACT

Evaluating the Impact of Ambient Benzene Vapor Concentrations on Product Water From Condensation Water from Air Technology Product Water:

MAJ Katherine Kinder, Master of Science in Public Health, 2016

Thesis directed by: Lieutenant Colonel Christopher A. Gellasch, Assistant Professor, Department of Preventive Medicine and Biostatistics, Occupational and Environmental Health Sciences Division.

Globally, available drinking water resources are diminishing in both quantity and quality. Growing concerns about water scarcity and drinking water shortages have renewed interest in Condensation Water From Air (CWFA) technology, which utilizes water vapor in the air to produce water for both potable and non-potable purposes. However, there is currently little data available to determine the relationship between air contaminants and the rate at which they are transferred from the air into CWFA product water. This study implemented a new experimental method to test a CWFA system in a controlled environmental test chamber in order to evaluate how air quality impacts the product water quality. Testing included target benzene vapor concentrations representing average outdoor polluted (50 $\mu g/m^3$) and indoor industrial (640 $\mu g/m^3$) settings as well as two temperatures (25˚C and 35˚C). Air and water samples were collected and analyzed for benzene. Characteristic of what Henry's Law concepts demonstrate, this study found that temperature and benzene air concentration affected the untreated product water from a CWFA system. In contrast to the conceptual similarities with Henry's Law, this study found enrichment factors of benzene concentration in the product water up to 2.1 times greater than what Henry Law calculations estimate. Benzene vapor concentrations representing a polluted outdoor environment resulted in benzene product water concentrations an order of magnitude below the U.S. military and USEPA drinking water standard of 5 µg/L. In contrast, benzene vapor concentrations representing an indoor industrial environment resulted in benzene product water concentrations up to 100% above the drinking water standard. Furthermore, air temperature significantly (p = 0.0001) affected the concentration of benzene in the product water, with lower temperature resulting in an increased benzene concentration in the product water. These findings indicate that both temperature and air quality should be taken into account during operation of CWFA systems as untreated product water quality will be affected by both factors at a rate that cannot be predicted by Henry's Law. Environmental health professionals and risk managers can integrate the results of this work to reduce potential exposure resulting from ingestion of contaminated water. The CWFA system manufacturers can integrate the results of this work to inform the appropriate level and maintenance interval of water treatment modules to minimize human health risk.

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ABBREVIATIONS

ACH	Air Changes per Hour
AH	Absolute Humidity
ANSI	American National Standards Institute
ARCIC	Army Capability Integration Center
ATSDR	Agency for Toxic Substances and Diseases Registry
ATM	Atmosphere
C	Celsius
CWFA	Condensation Water From Air
ECBC	Edgewood Chemical Biological Center
GC-MS	Gas-Chromatography-Mass-Spectrometry
g/m^3	Grams per cubic meter
HAP	Hazardous Air Pollutants
HCL	Henry’s Law Constant
HULIS	Humic-like Substance
ID	Inner Diameter
K_H	Henry’s Law Constant
LTP	Long Term Potability
M	Molecular Weight
MCL	Maximum Contaminant Level
MERV	Minimum Efficiency Reporting Value
mg/L	Milligrams per liter
Min	Minute

Mol/L	Moles per liter
NATA	National Air Toxic Assessment
NIOSH	National Institute for Occupational Safety and Health
NO_X	Nitric Oxides
OD	Outer Diameter
OEH	Occupational Environmental Health
OSHA	Occupation Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PEL	Permissible Exposure Limit
Pg	Partial Pressure
PID	Photoionization Detector
PPM	Part per Million
PPB	Part per Billion
®	Registered
REF	Rapid Equipping Force
RH	Relative Humidity
S	Solubility
SAS	Statistical Analysis Software
SIM `	Selected Ion Monitoring Mode
SVOC	Semi Volatile Organic Compounds
TARDEC	Tank Automotive Research Development and Engineering Center
TB MED	Technical Bulletin Medical
™	Trademark

TOC	Total Organic Carbon
TVOC	Total Volatile Organic Compound
TWA	Time Weighted Average
$\mu g/m^3$	Microgram per cubic meter
µg/L	Microgram per liter
USAIPH	United States Army Institute of Public Health
USEPA	United States Environmental Protection Agency
USUHS	Uniformed Services University Health Sciences
VP	Vapor Pressure
VOC	Volatile Organic Compound
WFA	Water From Air

CHAPTER 1: INTRODUCTION

BACKGROUND AND SIGNIFICANCE

The *United States Army Operating Concept: Win in a Complex World, 2020-2040* is a United States Army Training and Doctrine Command pamphlet describing a force that operates decentralized, distributed and integrated utilizing innovative systems and technology to operate in complex operational environments (9). The Army Capabilities Integration Center (ARCIC) identifies the Army's long range strategic priorities calling on the Army's Science and Technology community to reduce reliance on intermediate staging bases and sustainment forces by enabling combat units to be self-sufficient (2). In an effort to fulfill this need, the U.S. Army Tank Automotive Research, Development, and Engineering Center (TARDEC) is exploring the capabilities and applications of Water-from-Air (WFA) technology to the future force. The Program Manager, Rapid Equipping Force (REF) is exploring condensation WFA technology to rapidly issue to units in order to fill operational needs.

The WFA technology is attractive to the Army because it addresses two capability gaps: 1) The ability to bring water production close to the point of need, thereby reducing demand for extended logistical resupply; 2) The ability to produce water in areas in which other water sources are not readily available (3). These capability gaps are significant in operating environments that are remote and austere as well as the dense urban environment scenarios of future military operations. Envisioned WFA technology will close both capability gaps by improving the Army's ability to conduct expeditionary maneuver through increased water logistical efficiencies and thereby improve unit self-sufficiency.

The WFA technology has the potential to be used worldwide in outdoor (including industrialized, urban, rural, and naval) and indoor environments. Of the outdoor environments, the “dense urban environment” or Megacities maybe the most significant. Megacities are urban environments comprised of populations greater than 10 million or more. As of 2014, there are 28 megacities worldwide with an expected increase to 41 by 2030 (39). Since sixty percent of the world’s population is expected to live in urban environments by 2030, it is likely that future Army operations will occur in areas that are congested and highly polluted (9). Air pollution can have serious impacts on human health and can cause smog (20). Smog is the reactants and products of a series of complex chemical reactions between the oxides of nitrogen (NOx) and volatile organic compounds (VOC) in the presence of sunlight. The main primary pollutants are nitric oxide and hydrocarbons which are rapidly converted to secondary pollutants, ozone, organic nitrates, and oxidized hydrocarbons (32). Major sources of NOx and VOCs emissions include: industrial facilities, electric utilities, motor vehicle exhaust and gasoline vapors (49). In a 1996 study, Mage et al. (17) found that 20 of 24 megacities had air pollution levels where serious health effects were reported. Motor vehicle traffic was found to be a major source of emissions in all megacities, and the single most important source of emissions in half of the megacities. A more recent study by Gurjar et al. (11) evaluated three criteria pollutants (total suspended particles, sulfur dioxide and nitrogen dioxide) in 18 megacities and found that 5 megacities classify as “fair” air quality whereas the other 13 megacities classified as “poor” air quality.

Furthermore, many deployed military and civilian operations are conducted in indoor industrial settings. Many of these settings operate in conditions in which the indoor air quality has the potential to be extremely poor. Some examples of poor indoor air quality in military deployed settings include: storage of low grade petroleum products and pesticides as well as processes in automotive, paint, and armament shops. The military uses “JP-8” or Jet A-1 specification fuel as the primary source of fuel. This type of fuel is volatile and may be a significant source of inhalation exposure to Soldiers from toxic industrial chemicals when stored in an area with poor ventilation. Other indoor industrial operations conducted only in civilian settings include: coke plant processes and rubber tire manufacturing. Currently, there is limited instructions or special considerations for the prolonged operation and maintenance of the WFA water treatment systems in indoor industrial or polluted outdoor settings. Thus, it is important to characterize the water quality of drinking water produced from WFA technology in highly polluted outdoor and indoor industrial environments.

DRINKING WATER QUALITY

U.S. military personnel are deployed to various locations around the world with potential risk for Occupational and Environmental Health (OEH) exposures. Ingestion of drinking water is one exposure route in which Soldiers maybe exposed to health hazards. Adverse health risks from unsafe drinking water maybe acute or chronic in nature. Consumption of bacteriologically contaminated drinking water has an acute health risk, potentially posing an immediate health effect after one exposure. Consumption of low levels of VOCs or metals in drinking water over a long period of time have a chronic health risk, potentially posing health effects after a long exposure period. Therefore it is of utmost importance to ensure that drinking water is not only safe, but also promotes health, prior to consumption. To regulate the level of contaminants in drinking water, the United States Environmental Protection Agency (USEPA) has set standards for 90 chemical, microbiological, radiological and physical contaminants (46).

The WFA systems extract water from the air for both potable and non-potable purposes. In the United States, WFA system product water intended for drinking water purposes must meet the EPA drinking water standards. Furthermore, in a military deployed setting, WFA system product water must meet the military tri-service Long Term Potability (LTP) standards for military field drinking water, found in Technical Bulletin Medical (TB MED) 577 (2010). Currently, not enough information is available to determine the relationship between air quality contaminants and the rate at which they are transferred from the air into product water of WFA technology. As a result, there is uncertainty regarding the appropriate level of water treatment technology and the required maintenance interval of those components to ensure WFA systems meet the military tri-service LTP standards given a wide array of potential locations with different and changing/fluctuating air quality compositions.

WATER FROM AIR TECHNOLOGY

Water from Air technology utilizes water vapor in the air to produce product water. The concept is not new, with condensation WFA feasibility experiments dating back to 1969 (12). Given the high energy requirement to capture water from the air, it is a technology that is most attractive in situations in which water is expensive or not available due to source of infrastructure limitations. Given growing global concerns about water scarcity and drinking water shortages, momentum for this technology has grown. Currently, WFA technology is used for both potable and non-potable applications. As Walhgren (53) highlighted, the technology varies in scale and water production from small residential units, producing enough water to sustain an individual, to industrial sized units, producing enough water to sustain a neighborhood. The two most common types of WFA systems use either condensation or desiccant (liquid and solid) technology.

CONDENSATION WATER FROM AIR THEORY OF OPERATION

Condensation Water from Air (CWFA) Systems operate by condensing water vapor to form liquid droplets. CWFA systems accomplish the phase change from a vapor to liquid by cooling air to the dew point (wet bulb) temperature. The dew point is the temperature at which the air must be cooled in order to become saturated. Water vapor will condense to form liquid droplets below the dew point (or saturation) temperature.

Both temperature and humidity play an important role in the quantity of water produced by CWFA systems. Absolute humidity (AH) is expressed as the mass of water (g) in the air per the volume of the system (m^3). The higher the AH, the greater the moisture in the air. Thus, AH is an indication of the amount of moisture in the air, despite the air temperature. However, temperature also influences the amount of moisture in the air, as shown in Figure 1. Relative humidity (RH) is a measure of humidity that is temperature dependent and expressed as a percent of saturation. It is the ratio of water vapor in a volume of air per the amount of water that would be present if the air was saturated at the same temperature. Consequently, high temperature and absolute humidity values have high moisture holding capacity in the air. Therefore, temperature and absolute humidity effect the quantity of water produced by CWFA system. An example of this relationship is shown in Table 1. Theoretically, and dependent on the efficiency and design, a CWFA system producing water at an air temperature of 25˚C and 65% RH may produce half the product water than the same system at an air temperature of 35˚C and 65% RH since the latter values result in a higher absolute humidity (15 g/m^3 vs 26 g/m^3). Likewise, the same system producing water at an air temperature of 35˚C and 45% RH will produce more water than operation at an air temperature of 25˚C and 65% RH since the former values result in a higher absolute humidity (18 g/m^3 vs 15 g/m^3).

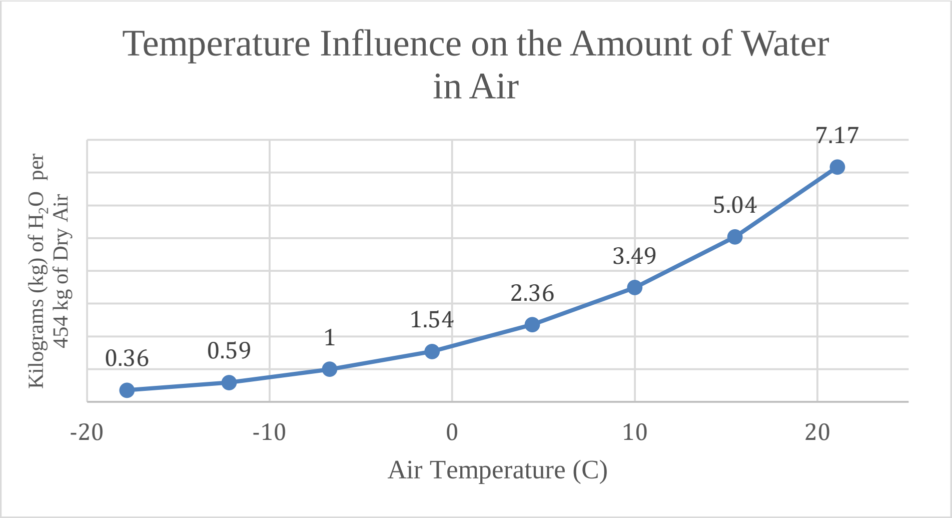

Figure 1. Temperature Influence on the Amount of Water in Air (42)

Table 1. Absolute Humidity (g/m^3) Given Temperature and Relative Humidity.

Temperature (C)	Relative Humidity 45%	Relative Humidity 65%
25	10	15
35	18	26

As shown in Figure 2, major components of CWFA systems are the compressor, condenser coils, evaporator, filter for the inlet air, fan and a liquid medium. These components are essential to the vapor compression cycle and process air flow that drive the cooling process for the CWFA system. It is important to note that not all condensation systems are the same. Condensation systems vary in design for improvements in energy efficiency and water treatment. Nevertheless, the core process is very similar in most condensation technologies. In addition to the essential components, most CWFA systems have the following components: a water storage tank, a pump, piping and water treatment system.

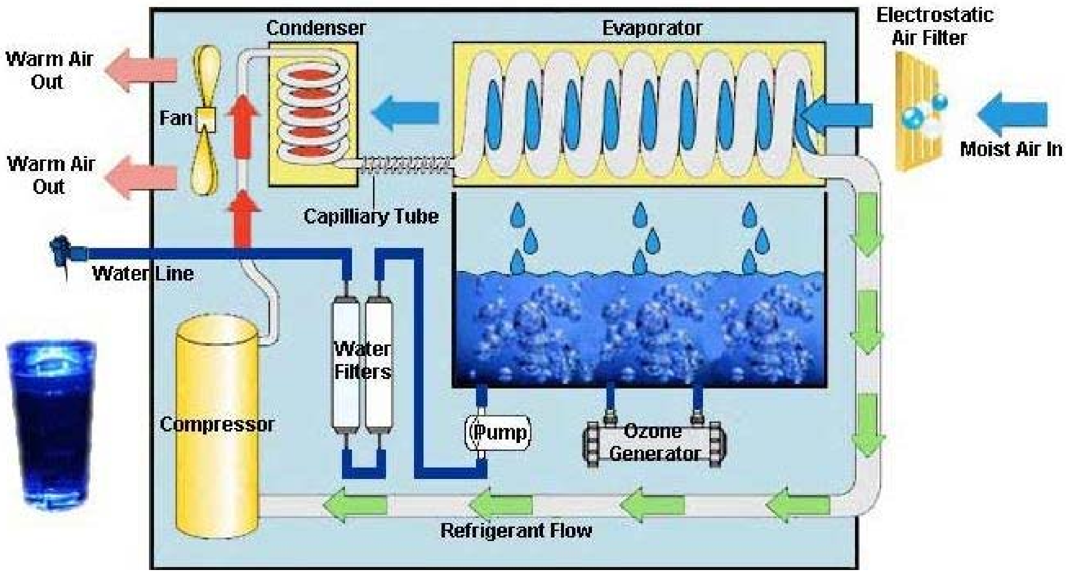

Figure 2. CWFAS Process Flow Diagram (28)

The process of making drinking water from air starts when ambient air is drawn into the CWFA system by a fan that pulls air through an air filter. The purpose of the air filter is to remove particles from the ambient air to keep the surfaces on the evaporator coils clean (53). Next, the ambient air is pulled across the evaporator coils. It is on the evaporator coils of the refrigeration cycle that process air is cooled to the dew point and water vapor condenses to form liquid droplets. Water that forms on the evaporator coils is collected in a water storage tank. Excess heat that is generated as a result of the compression of the refrigerant is then removed from the system by a fan as the cooled air passes over the refrigeration condenser coils. For systems designed for drinking water purposes, product water leaves the water storage tank through a piping system made from material appropriate for potable water in accordance with NSF International/American National Standards Institute (ANSI) 61. Lastly, the product water is treated prior to leaving the system. A few examples of treatment technology that may be used on the CWFAS include: disinfection by an ultraviolet light; reduction/removal of total dissolved solids, micro-organisms, and organic chemicals by reverse osmosis; removal of organic chemical by a granulated carbon filter; removal of particulates by a sediment filter; or a combination of water treatment technologies. Water treatment type is chosen by the manufacture and is diverse across the industry. Of the water treatment technology listed above, reverse osmosis is the most protective; however, has two major disadvantages as a WFA water treatment technology: it requires a significant amount of energy to operate (adding to an already extensive energy requirement) and creates membrane reject water, reducing the quantity of available product water and creating water that is not potable.

Often the saturation temperature is lower than the ambient air temperature. The compressor, condenser, evaporator and a liquid medium (chilled water and/or a refrigerant) in the CWFAS are the primary components that create the conditions to lower the process air temperature to the saturation temperature. Liquid medium type depends on the design of the CWFAS. Standalone refrigerant use is for systems that receive a small amount of airflow, such as a residential use (53). Refrigerant combined with a chiller medium (water or brine) is used when larger air volumes are processed, such as in an outside environment or in an industrial setting (53). Refrigerant (most commonly the hydrofluorocarbon R-134a) is used in a vapor compression cycle that is very similar to what takes place in a refrigerator. The vapor compression cycle uses pressure in a closed loop system to manipulate the refrigerant from a gaseous to liquid state to keep the temperature of the evaporator coils at a set temperature that is below the saturation point.

PAST WATER FROM AIR STUDIES

The WFA technology has the potential to be used worldwide in a variety of environments. To date, not enough information is known to determine the relationship between air quality contaminants and the rate and quantity at which they are transferred from the air into water through the CWFAS. Walhgren's (53) review on WFA technology indicated water produced from the atmosphere may not be safe to drink without treatment. Gandhiasan and Abualhamayel (10) specify that in polluted urban and industrial environments, water quality of desiccant WFA systems may be compromised and should be monitored. Studies by Walhgren, Gandhidasan and Abualhamayel, and Loveless et al. (10, 16, 53), tested water quality of WFA systems for limited metals, chemical and physical parameters (summarized in Table 2). All tested parameters in these studies were found within drinking water standards; however, the air quality in which the systems were operated was not documented.

An unpublished study by the U.S. Army Institute of Public Health (USAIPH) performed a risk characterization of untreated and treated product water from a desiccant WFA system (37). Untreated and treated water parameters included total coliforms, metals, semi-volatile organic compounds (SVOCs), VOCs, inorganic chemicals, and various physical characteristics. Results from untreated water in this study indicated that Di (2-ethylhexyl) phthalate and bacteriological samples exceeded the EPA drinking water standard while all other tested parameters were within standards. Bacteriological contamination was most likely the result of contamination of the condensate collection vessel and/or the presence of bacteria in the air that transferred to the untreated product water; however the report did not mention the source of contamination. Additionally, the report did not indicate the source of Di (2-ethylhexyl) phthalate contamination. However, the treated product water met the drinking water standard for Di (2-ethylhexyl) phthalate. Like previous studies, the USAIPH assessment did not include ambient air samples to quantify data about ambient air quality in which water quality testing was conducted. Without quantifiable information about the air quality to compare against water quality data, it is difficult to determine the relationship between the product water quality and ambient air quality.

Since the raw water source from CWFAS is drawn from the air it is appropriate to test different air quality environments to determine how product water quality is affected. A study by Bautista-Olivas et al. (6) demonstrated that heavy metals present in the ambient atmosphere of polluted urban cities can transfer from the air to the product water of condensation WFA systems at levels above the permissible exposure limits for drinking water.

A review of current literature found no studies quantifying VOC concentration in product water from a polluted air environment. However, a study conducted by Okochi, et al. (26) demonstrated that total humic-like substances (HULIS) in dew water may enhance the dissolution of VOCs into dew droplets. The researchers found that enrichment factors, defined as the ratio of the observed VOC concentration in dew water to the calculated value, increased as HULIS concentration increased. Enrichment factors found in this study were attributed to a decrease in surface tension and significantly correlated to the concentration of HULIS in dew water. Since the Okochi et al study found that VOC air concentration and content affects dew water, it is possible that VOC air concentration and content will affect the untreated product water of CWFA systems. Thus, there is a knowledge gap and a need to conduct research to investigate how VOC air quality will affect the product water quality of CWFAS.

Table 2. Summary of Product Water Quality of WFA Systems

Author, Date	**Water Quality Parameter**	**Air Data**	**Water Results**
Walhgren (2000)	Nitrate, Nitrite, Lead, Copper, total coliform, *E. Coli*	None provided	All within EPA drinking water standards
Gandhidasan and Abualhamayel (2010)	Multiple Chemical Parameters	None provided	All within EPA drinking water standards
USAIPH (2011)	Total coliforms, *E. Coli*, metals, SVOCs, VOCs, Inorganic chemicals, physical parameters	None provided	Raw water Di (2-ethylhexyl) phthalate and E. Coli exceeded standards
Loveless et al. (2013)	pH, conductivity and turbidity	None provided	All within EPA drinking water standards
Bautista-Olivas et al. (2014)	Conductivity, Al, As, Ba, Cd, Cu, Cr, Fe, Hg, Mn, Pb and Zn,	Product water samples taken in three urban cities, specific air data not provided	Some samples exceeded the regulatory limits for Al, Fe and Pb

The WFA technology has the potential to be used in industrialized, urban, rural, naval, and indoor environments as a source of drinking water for the military. Therefore, it is important to characterize these types of environments. Concentrations of a contaminant of concern that is representative of a highly polluted urban environment (megacity) and indoor industrial environment will be used to challenge the condensation WFA system in an environmental chamber. This study is the first of its kind to determine how air temperature and airborne contaminant concentration influence the concentration of contaminant in the untreated product water of CWFA systems.

SELECTION OF THE CONTAMINANT OF CONCERN AND AIR CONCENTRATION LEVEL

There is a plethora of VOCs that could be potentially hazardous to human health. Since the contaminant of concern will be tested in a controlled environment, this research is limited in time and resources to just one of the most likely and most severe VOCs that may affect human health via ingestion. To select the most likely and severe contaminant, this study examined the EPA's 2005 National Air Toxic Assessment (NATA). The EPA's NATA provides information on 177 of the 187 hazardous air pollutants (HAPs) and prioritizes the pollutants and emission sources around the U.S (47). The EPA 2005 NATA prioritized national and regional cancer drivers and contributors as well as non – cancer drivers and contributors into high, medium and low risk categories. The EPA NATA lists four high priority national/regional *cancer drivers* (benzene, formaldehyde, naphthalene, benz(a)pyrene).

Next, EPA's National Primary Drinking Water standards were compared to the high priority VOC cancer risk drivers, where available, to identify pollutants that were common to both lists (46). Formaldehyde and naphthalene did not have an USEPA drinking water maximum contaminant level (MCL) based on a health risk assessment for ingestion and were not further considered for this evaluation. Of the remaining two high priority contaminants, benz(a)pyrene was not chosen because it is difficult to detect in real time at ambient air levels. Benzene (C_6H_6) is the chosen contaminant of concern for this study primarily because of its physical characteristics, likelihood of presence at deployment sites and potential health effects. Benzene (Figure 3) is a colorless aromatic liquid that is present at low levels in the ambient air around the world (1).

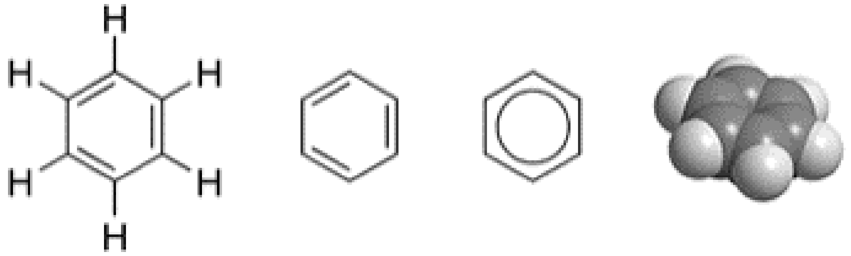

Figure 3. Benzene (C6H6) Structure (36)

Ambient air concentrations of benzene vary significantly across the globe. To determine an appropriate benzene test concentration, a literature search of global ambient benzene concentrations in urban and industrialized areas was conducted (Table 3). The literature revealed a high variation of benzene levels in urban and industrial areas across the globe with the highest levels of benzene found in India. Srivastava et al. (35) monitored benzene levels in Mumbai, India at residential, industrial, commercial, traffic intersections and petrol stations measured during peak hours of the day. They found that benzene air concentrations were highest at petrol stations with a mean of 539.95 micrograms/per cubic meter (µg/m^3) and lowest in residential areas with a mean of 45 µg/m^3. Other studies conducted in China, Japan, Egypt, U.S. and Korea indicate a much lower range of benzene levels across the globe ranging from 0.2 µg/m^3 in Japan to 87.2 µg/m^3 in Egypt (5, 14, 15, 21, 24, 35, 54). Given the wide array of benzene concentrations found in the literature, this study targeted 50 µg/m^3 to represent a global average benzene level for a polluted outdoor urban/industrial environment.

Table 3. Summary of Benzene Ambient Air Levels in Urbanized/Industrialized Environments

Author, Date	Location	Ambient Concentration (μg/m^3)
Liu et al. (2000)	Changchun, China	Roadside 38.5 Downtown 43.8 Industrial 22.3 Inhabited 20.6
Na et al. (2001)	Ulsan, Korea	6.7 (average)
Batterman et al. (2002)	Detroit, Michigan United States	4.5 (geometric mean)
Srivastava, Joseph, & Devotta, (2006)	Mumbai, India	45.31 Residential 539.95 Petroleum pumps
Ohura, Amagai, & Fusaya (2006)	Shizuoka, Japan	Summer: 0.48 (geometric mean) Winter: 0.95 (geometric mean)
Khoder (2007)	Cairo, Egypt	87.2 (mean)
Wang & Zhao (2008)	Nanjing, China	6.4

In a military deployment setting, Army personnel conduct refueling operations, automotive repair, weapons cleaning, and painting operations in indoor and outdoor settings. When these operations are conducted indoors, air quality has the potential to be extremely poor. Although refueling operations are not conducted indoors, a service station maybe partially covered and limit the amount of circulation in the refueling area. To determine an appropriate benzene test concentration in an indoor industrial setting, this study examined the regulatory and recommended limits for benzene in an occupational setting as well as the literature for recorded concentrations of benzene in indoor industrial settings.

The Occupational Safety and Health Administration (OSHA) is a United States government run public health agency that focuses on worker safety (23). In 1987, OSHA lowered the permissible exposure limit (PEL) - time weighted average (TWA) of airborne benzene from 10 parts per million (ppm) to 1 ppm (3,194 µg/m^3). The action level for benzene is 0.5 ppm (1,597 µg/m^3), the level at which steps must be taken to reduce worker exposure. Therefore indoor industrial levels of benzene should be below 1 ppm. However, the National Institute for Occupational Safety and Health (NIOSH) recommended a much more conservative exposure limit for benzene of 0.1 ppm (319 µg/m^3) (22).

The literature indicates that air concentrations of benzene associated with fueling, automotive, painting and cleaning operations also have large variations (Table 4). Many factors may affect the concentration of benzene including: environmental conditions such as temperature and humidity, control measures such as appropriate ventilation and enclosure type, the length of the task, and whether it is continuous or intermittent (31). Refueling and painting operations had the largest variation with a range of 144.5 – 1731 µg/m^3 and 100 – 47000 µg/m^3 respectively (8, 34, 52). The highest levels in painting operations were noted in shops in which safety precautions were not followed in order to expedite operations (52). Given the wide range of indoor industrial benzene levels for the designated operations, this study will target 640 µg/m^3 to represent an indoor industrial setting.

Table 4. Summary of Benzene Air Concentrations in Indoor Industrial Settings

Author	**Facility Type**	**Occupation/Activity**	**Benzene Concentration ($\mu g/m^3$)**
Soldatos, Bakeas, & Siskos, (2003)	Service station	Gasoline fueling	1,731
Vitali et al, (2005)	Car painting workshop	Painting	100 – 47,000
De Oliveira et al. (2007)	Service Station	Fueling Operations	144.5
Sheehan et al. (2010)	Service Station Auto repair	None Provided	7,040 704
Sheehan et al. (2010)	Recycling Facilities	Parts Washing	108.8 - 416

PHYSICAL PROPERTIES OF BENZENE AND HENRY'S LAW

Benzene's fate and transport into the environment can be predicted from its physical properties, presented in Table 5. Important to this study is the expected transport of benzene from the air to the product water of CWFAS; which is influenced by benzene's solubility and vapor pressure. Benzene is considered highly volatile with a vapor pressure of 95.2 mm Hg at 25˚C and moderately soluble with a solubility of 1,780 mg/L at 25˚C. Thus benzene in water is subject to rapid volatilization from water to the air at a rate that is temperature dependent. Henry's Law constant and equation can be used to predict the amount of benzene that maybe present in drinking water given benzene air concentration and temperature.

Table 5. Physical Properties of Benzene (38)

Property	**Information**
Molecular Weight	78.11 g/mol
Boiling Point	80.1C
Solubility	1790 mg/L @25C
Vapor Pressure	94 mm HG @ 25˚C
Biodegradation half-life	16 days
Log Kow	2.13
Henry's Law Coefficient	0.0055 atm-m3/mol @ 25˚C
Molar enthalpy of vaporization	33.83 kJ/mol

Henry's Law

William Henry formulated "Henry's Law" in 1803 that states at a constant temperature, the amount of gas that is dissolved in a solvent is directly proportional to the partial pressure of that gas and concentration in the water (7). Each chemical has a Henry's Law constant that is indirectly derived from the relationship of the chemical's vapor pressure to the chemical's solubility (33). There are many forms of Henry's Law constant equation. This paper will use the following equation (EQ) below (41):

$$HLC = (VP)(M)/(S) \quad [EQ \#1]$$

In which:

HLC = Henry's Law constant (atm-m^3/mol)
VP = vapor pressure (atm)

M = molecular weight (g/mol)
S = solubility (mg/L or g/m^3).

Henry’s Law constant can then be applied to the Henry’s Law equation, expressed as (19):

$$[\mathrm{gas}] = K_H\,(Pg) \qquad [\mathrm{EQ}\ \#2]$$

In which:

[gas] = moles of gas per liter of solution (mol/L)
K_H = Henry’s Law constant (mol/L*atm)
Pg = Partial pressure of the gas (atm) above the solution

Temperature is an important consideration for Henry’s Law. While not apparent in the equations above, temperature is embedded within the vapor pressure and solubility values. Therefore Henry’s Law “constant” is more accurately referred to as a “coefficient” since the value changes with temperature (33). Solubility and vapor pressure values have been empirically derived from experiments at a constant temperature and pressure, most often valued at 25˚C and 1 atmosphere (ATM). Therefore the use of K_H at 25˚C and 1 ATM when actual temperature or pressure values are greater or less, may lead to significant error in calculations (33). Often not available for temperature values other than 25˚C and 1 ATM and must be calculated using empirical data to determine the appropriate coefficient per temperature and atmospheric pressure value. In order to obtain temperature adjusted K_H, the following equation can be used (48):

$$H_{TS} = H_R \exp\left[\frac{-\Delta H v,TS}{Rc}\left(\frac{1}{Ts} - \frac{1}{TR}\right)\right] \qquad [\mathrm{EQ}\ \#3]$$

In which:

H_{TS} = Henry's coefficient (atm-m^3/mol) at the Kelvin (K) temperature

T_S = required temperature

$\Delta H_{v, TS}$ = is the enthalpy of vaporization at T_S in units of cal/mol

T_R = is the reference temperature for Henry's Law (H_R) in K

R_C = the gas constant and is equal to 1.9872 cal/mol-K.

Since product water from the CWFA system condenses on the evaporator coils at or below the saturation temperature, the amount of water vapor in the air influences the temperature of the product water. Saturation temperatures are shown as a function of relative humidity and air temperatures in Table 6. Additionally in Table 6 (given EQ 1 and 3) are K_H given experimental (25˚C and 35˚C) and saturation temperature values (at 65% and 45% relative humidity). The highest K_H value (mol/atm-L) corresponds with the lowest temperature. Since the relationship of K_H values to the partial pressure of the air is multiplicative (EQ 2), higher K_H values will result in higher concentration of benzene in the water given the same benzene air concentration.

Table 6. Temperature adjusted K_H

Temperature (° C)	K_H (mol/atm-L/)
25	1.799 E-01
35	1.164 E-01
18 (25˚C @ 65% RH)	2.506 E-01
27 (35˚C @ 65% RH)	1.642 E-01
12 (25˚C @ 45% RH)	3.390 E-01
21 (35˚C @ 45% RH)	2.167 E-01
Light Blue: Air Temperature Values Light Grey: Saturation Temperature Values	

Accordingly temperature maybe an important factor in the concentration of benzene in the product water of CWFA systems. Benzene in ambient air may transfer to the product water of CWFA systems in greater concentration at lower temperatures and be present in water long enough to be ingested by the consumer.

HEALTH EFFECTS: BENZENE

Sources of benzene include both anthropogenic and natural sources. According to the Agency for Toxic Substances and Diseases Registry (ATSDR), anthropogenic uses of benzene are primarily as a chemical in industry, as a starting material in the creation of other chemicals and as a gasoline additive (1). Additionally, benzene is found in a multitude of consumer products such as paint solvents and thinners, solvents, petroleum distillates, rubber and cement. Natural sources include forest fires, crude oil seep and plant volatiles. Given the large amount of natural and manmade benzene in the environment, everyone is exposed to small amounts every day. According to the ATSDR, inhalation is the primary route of exposure to the general population (1). With the two main U.S. sources of inhalation exposure being smoking tobacco (50%) and auto exhaust and industrial emissions (20%) (1). Additionally, since benzene is moderately soluble in water, it is not surprising that it is present in small amounts as background levels in ground and surface water as well as food products (1).

The primary route of exposure examined in this study is the oral ingestion of benzene from drinking water. The ATSDR summarizes multiple animal and a few human studies that describe in the absorption, distribution, metabolism, and excretion (ADME) of benzene when introduced into the body from the oral route. When benzene is orally ingested it is absorbed by the gastrointestinal system and passes through the gastrointestinal track to enter the bloodstream. Once in the bloodstream, benzene travels throughout the body and can be temporarily stored in the bone marrow or fat. Benzene is converted to metabolites primarily in the liver via the first pass effect and secondarily in the bone marrow. The first step in benzene metabolism in the liver is the cytochrome P-450 2E1 catalyzed oxidation reaction of benzene to form benzene oxide. Thereafter, the primary pathways to benzene metabolites include cytochrome P-450 2E1 and glutathione, with multiple secondary pathways. Some metabolites of benzene include: 1,2- and 1,4-benzoquinone to catechol and hydroquinone, 1,2,4-benzenetriol, and S-phenylmercapturic acid. Since benzene toxicity is expressed as metabolites, it is significant that a higher percentage of metabolites are excreted at high level benzene exposures than low level benzene exposures. Low level benzene exposures are quickly metabolized and excreted primarily in the urine. At high benzene exposure levels, metabolic pathways appear to become saturated and a large portion of an absorbed dose of benzene is excreted as exhaled air. Available data suggests that benzene metabolites produced in the liver and not immediately excreted are carried to the bone marrow from which benzene toxicity is expressed (1).

The ATSDR describes the health effects associated with oral exposures to benzene as described below and summarized in Table 7 (1). Health effects of benzene result from acute, sub-chronic and chronic exposures. Non-target organ effects for oral benzene exposure include genotoxicity and carcinogenicity. As such, benzene is classified as a genotoxic carcinogen. The primary target organs for oral exposures are the gastrointestinal, hematopoietic, nervous, and immune systems. With chronic exposures having the greatest effect on the immune and hematopoietic system due to benzene metabolite effects on the bone marrow. The most severe health effect is death as a final outcome from acute, sub-chronic or chronic exposures of benzene. Less severe effects include neurological (memory less, distal neuropathy and difficulty sleeping) and gastrointestinal (toxic gastritis and pyloric stenosis) health effects (1).

The most significant health effect of benzene is that it is a carcinogen. Acute non-lymphocytic leukemia has been causally associated to occupational inhalation exposures to benzene. Additionally, some studies suggest a linkage between benzene inhalation exposure and non-Hodgkin's lymphoma and multiple myeloma. At this time there is no information regarding the oral carcinogenicity of benzene in humans. However, there have been several animal studies indicating benzene as a multiple site carcinogen by the oral route (13, 18). A study by Huff et al. (13) examining rats and mice found that multiple sites of cancer included: Zymbal gland carcinomas, lung aleolar/bronchiolar adenomas and carcinomas, mammary gland carcinomas in females, and harderian gland adenomas in males.

Table 7. Benzene Health Effects Associated with Oral Exposure as Summarized by ATSDR

Health Effect		**Exposure Period**	**Type of Study**	**Symptoms**
Genotoxic		Chronic	Animal and Human	Chromosomal aberrations
Systemic	Hematological	Sub-chronic, Chronic	Animal	Decrease in erythrocytes and leukocytes
	Gastrointestinal	Acute	Human	Toxic gastritis and pyloric stenosis
Neurologic		Acute, Sub-chronic, and Chronic	Human	Memory loss, distal neuropathy and difficulty sleeping, peripheral nervous system effects
Immunological and Lymphoreticular Effects.		Sub-chronic and Chronic	Animal and Human	Damage to antibody and leukocyte responses
Carcinogenic		Chronic	Animal	Leukemia and multiple site carcinogen (in animals)

Given the wide range of potential health effects from the oral ingestion of benzene, the EPA has set the maximum contaminant level (MCL) for benzene in drinking water at 5 µg/L. However, since it is a carcinogen, the EPA's public health goal for benzene in drinking water is zero (46). Given the potential severe health effects of benzene from oral exposure routes, due diligence to determine how air temperature, humidity and airborne benzene concentration influence the concentration of benzene in the untreated product water of CWFA system is needed.

PURPOSE AND HYPOTHESIS

This research will explore benzene as a contaminant of concern that is common to urban and industrial environments across the globe. Benzene concentrations representative of a highly polluted outdoor urban environment and indoor industrial environments will be used to challenge the CWFA system in an environmental chamber. This study is the first of its kind to determine how air temperature and airborne benzene concentration influence the concentration of benzene in the untreated product water of CWFA systems. Results from this research will inform the health risk assessment, selection of appropriate treatment technologies and maintenance considerations for future WFA technologies. This will ultimately lead to the prevention of potential health risk exposures as a result of the ingestion of contaminated drinking water by service members.

OBJECTIVE AND SPECIFIC AIMS

Objective:

Exploratory investigation of the relationship of benzene air concentration and temperature with the concentration of benzene in untreated product water of CWFA systems.

Hypothesis #1: When benzene is present at levels common to current polluted urban outdoor environments it will transfer from the air to the product water at levels that are *below* the maximum concentration level for drinking water standards.

Hypothesis #2: When benzene is present at levels common to current indoor industrial environments it will transfer from the air to the product water at levels that are *above* the maximum concentration level for drinking water standards.

Specific Aim 1: Model the expected product water quality using Henry's Law to determine the estimated mass of benzene that may transfer from ambient air to product water and the resulting concentration in the water.

1) Apply Henry's Law to calculate expected concentrations for benzene using multiple temperature (ambient air and saturation) values in order to apply the appropriate method for water analysis.
2) Compare results against the EPA MCL for benzene in drinking water to assist in planning for pilot and full scale sampling operations.

Specific Aim 2: During a pilot test in an environmental chamber, conduct benzene sampling of the air and product water at a moderate temperature of 25˚C, relative humidity of 65% and benzene concentration of 50 µg/m^3.

1) The pilot test will be used to determine variation in the experiment and to determine appropriate sample size for the full scale test.
2) Compare water sample results to EPA MCL for benzene in drinking water.

Specific Aim 3: During the full scale test, conduct benzene sampling of the ambient air and product water at two concentrations of benzene 50 µg/m^3 (representing a polluted outdoor urban environment) and 640 µg/m^3 (representing an indoor industrial environment).

1) Compare water sample results to EPA MCL for benzene in drinking water.

2) Perform descriptive statistics to determine if water sample results follow a normal distribution. Given a normal distribution, the t-test will be used to determine if there was a significant difference between the means of the untreated product water of CWFA systems and the EPA benzene MCL for drinking water.

Hypothesis #3: Changes in temperature influence the accumulation of benzene in product water of the CWFA system.

Specific Aim 4: During the full scale test, conduct ambient air and untreated product water sampling at 35˚C and 25˚C at a steady state relative humidity of 45%.

1) Compare water sample results to EPA MCL for benzene in drinking water and expected contaminant levels (calculated from Henry's Law equation).
2) Compare indirect reading air samples to direct reading air samples. If concentration levels fluctuate, compare water sample results to indirect reading air sample results.
3) Compare untreated product water concentrations of benzene to that of the control concentrations and calculated values in order to correlate whether the ambient air or saturation temperature is the controlling temperature and mechanism for Henry's Law values.

Hypothesis #4: There is an increase in the concentration of benzene in the untreated product water compared to the control.

Specific Aim 5: During the full scale test, conduct sampling of both the untreated product water and control water and analyze for benzene concentration.

Perform descriptive statistics to determine if water sample results follow a normal distribution. Given a normal distribution, the t-test will be used to determine if there was a significant difference between the means of the control and untreated product water of CWFA systems.

CHAPTER 2: METHODOLOGY

STUDY DESIGN

This quantitative research tested a CWFA system in a controlled environmental test chamber in order to evaluate how air quality impacts the product water quality. Testing was conducted at the U.S. Army Edgewood Chemical Biological Center (ECBC) located at Edgewood Area of Aberdeen Proving Ground in Edgewood, Maryland. Average outdoor polluted (50 µg/m^3) and indoor industrial (640 µg/m^3) benzene air concentrations as well as temperature (25˚C and 35˚C) were tested using a 2 x 2 factorial guided design of experiments. Air and water samples were collected and analyzed for benzene. Water samples consisted of a product and control sample. Concentrations of benzene in the product and control water were compared to each other, benzene air concentration and temperature data. This research was conducted in two phases; the pilot and full scale phase. The pilot phase was used to determine the coefficients of variance of the experiment and appropriate sample size for the full scale phase. This study was conducted at 80% power with an alpha = 0.05 level of significance.

EXPERIMENTAL SET-UP AND MATERIALS

A commercially available CWFA system was selected for untreated product water tests. The AquaBoy™ was selected for test because of its size, water generation rate, and price. The AquaBoy™ is a residential or office building CWFA system that is 0.38 m (width) x 0.48 m (length) x 0.52 m (height). The AquaBoy™ is electrically powered and weighs 39 kg (85.8 pounds (lbs)). The height and weight of this system was appropriate to fit inside of the environmental chamber. The refrigeration cycle in this unit utilizes refrigerant R134a. This unit has an electrostatic air filter to remove particle matter from the air.   Figure 4 shows the manufacture's process flow of diagram of AquaBoy™ unit. In preparation for test a number of modifications were made to the AquaBoy™. The most significant modification was the removal of the water treatment module. According to the manufacturer the water treatment module was comprised of a sediment, charcoal and ultra-fine membrane and Halo Pure cartridge. Other components such as the system's pump, solenoid, and untreated water reservoir were removed to provide additional space for the test's product water collection beaker and to prevent potential unintended contamination of the untreated product water. Lastly, a Dickson thermocouple temperature logger (Model KT802) was secured to the outer evaporator coil in the AquaBoy in order to monitor and track coil temperature.

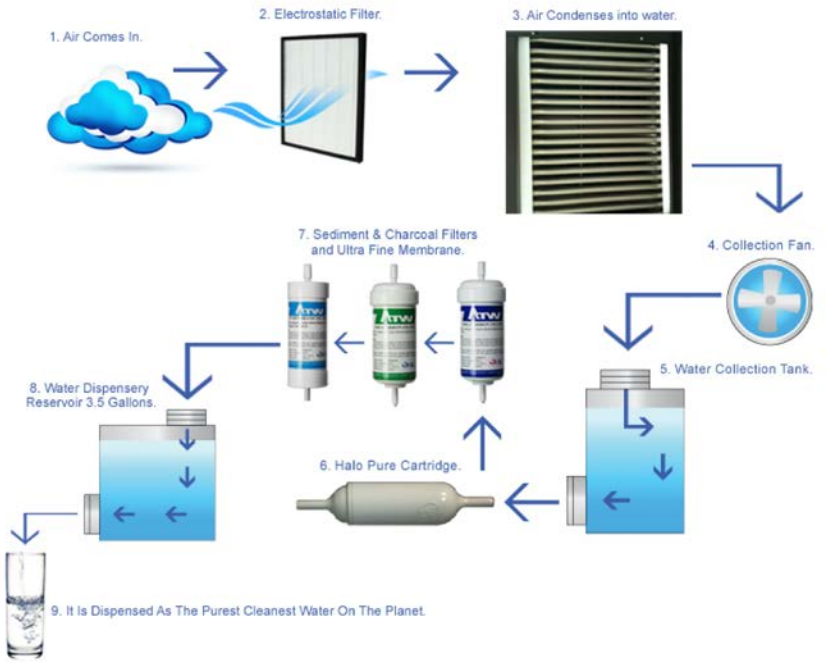

Figure 4. Manufacturer's Process Flow for the AquaBoy™ (4)

An environmental chamber was utilized to maintain benzene, temperature, and relative humidity at steady state conditions. Two different stainless steel environmental chambers were used for the pilot and full scale tests. For the pilot test, the environmental chamber measured 2.3 m (7.41 feet) length x 1.2 m (4 feet) depth x 1.2 m (4 feet) height or 3.0 m^3 adjusted for equipment in the chamber. The chamber had multiple access points including one sampling port door, one sample port hole, a main door, and two sets of hand inserts (one on each side). The pilot chamber was supplied with indoor air that was not further filtered at a flow rate of 97 air changes per hour (ACH). The environmental chamber for the full scale test measured 2.6 m x 1.1 m x 1.2 m or 3.1 m^3 adjusted for equipment in the chamber with the same number of access points in a different configuration. Figure 5 shows a schematic diagram of the environmental chamber set up for the full scale test. The full scale chamber was supplied with indoor air that was not further filtered at a flow rate of 81 air changes per hour (ACH). Due to the nature of environmental chamber design for chemical and biological tests, the ACH rate was not controlled by the operator. Relative humidity in both chambers were automated and controlled by dehumidification coils and a vapor generator. The tap water used to generate humidity was filtered through a carbon filter to remove organic impurities prior to entering the chamber. Temperature in the chambers was also automated and controlled by refrigeration and nichrome heating elements. A calibrated Vaisala HUMICAP® hand held humidity and temperature meter (model number HM141) was placed inside the chamber to track and monitor relative humidity and temperature readings every five minutes during test to verify they were within the target ranges.

Benzene contained in a certified compressed gas cylinder containing 0.322 m^3 of 1.01 MOLE % concentration benzene (HP GAS LLC) was introduced into the chamber at a pressure of 1.266 kilograms per square centimeter and a rate controlled by a calibrated, Seirra, mass flow controller (Smart-trak®, 10-50 cubic centimeter (cc) /minute (min)). The benzene cylinder was connected to a mass flow controller by 3.18 mm outer diameter (OD) straight Teflon tubing with 3.18 mm Swagelok tube fittings. Additional Teflon tubing was routed from the mass flow controller through the sample port door of the chamber. Inside the chamber, a Teflon tubing network consisting of six legs was mounted evenly across the chamber in order to uniformly distribute benzene within the chamber.

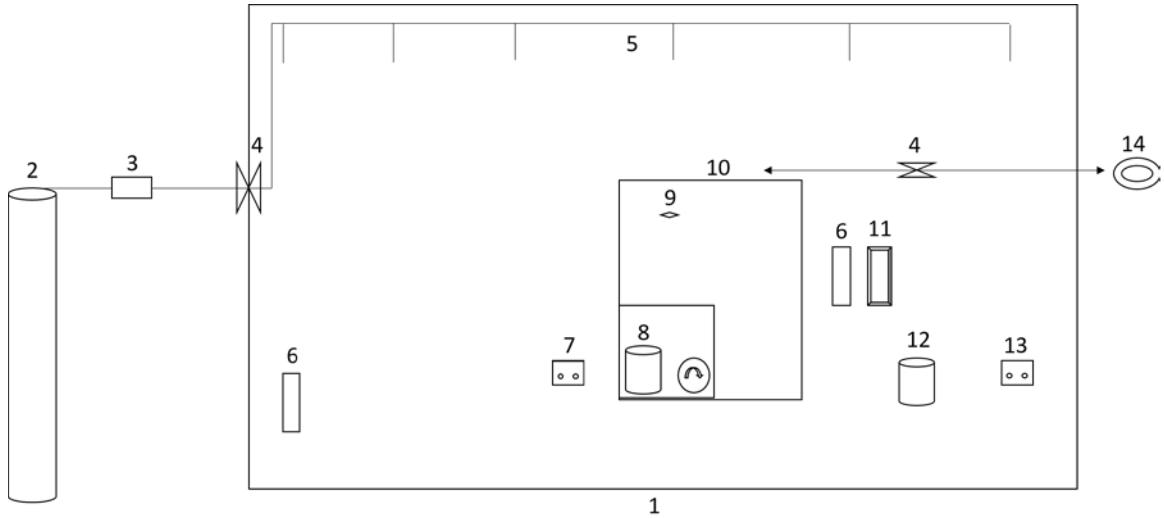

Figure 5. Schematic Diagram of the Environmental Chamber Set-up. 1. Environmental chamber, 2. Benzene gas cylinder, 3. Mass flow controller, 4. Chamber access point, 5. Teflon tubing network, 6. PPB PIDs, 7. Product water collection vials, 8. Product water collection beaker, 9. Thermocouple, 10. CWFA system, 11. Humidity and temperature meter, 12. Control water beaker, 13. Control water collection vials, 14. Summa canister

EXPERIMENTAL PROCEDURE

This study was conducted in two phases: the pilot and full scale. The primary purpose of the pilot test was to determine variation in the experimental method and calculate an appropriate sample size for the full scale test. Additionally, the pilot test was used to implement a new experimental method to test the product water of CWFA system in known benzene vapor concentrations. The full scale test implemented improved experimental procedures learned during the pilot tests and expanded upon the experimental test conditions. Air and water samples were collected during discrete one hour sampling rounds and analyzed for benzene. A summary of pilot and full scale tests is shown in Table 8.

Table 8. Summary of Pilot and Full Scale Tests

Test	Type of Test	Benzene Concentration (μg/m^3)	Temperature (°C)	Relative Humidity (%)	Discrete 1 hr Sampling Rounds
Pilot 1	Verification of temperature and RH	None	15.5 - 35	45 - 90	NA
Pilot 2	Steady state Test	50	25, 35	45, 65	NA
Pilot 3	Sample Size Determination	50	25	65	6
Pilot 4	Sample Size Determination	50	25	65	6
Condition 1	Full Scale	50	25	45	6
Condition 2			35		6
Condition 3		640	25		6
Condition 4			35		6

The Pilot Phase

This study developed a new experimental method to test the product water of CWFA system at known benzene air concentrations. Table 8 provides a summary of the pilot phase tests. The pilot phase consisted of Henry’s Law calculations and four separate pilot tests in an environmental chamber. Henry’s Law calculations were used to determine the theoretical benzene concentration in control and product water given a temperature, relative humidity and known concentration of benzene in the air. Analytical method planning utilized the calculated values to ensure that benzene concentrations in the water were at levels that could be detected by the analytical methods. Additionally, revised calculated values based on the test condition mean coil and air temperature and mean benzene vapor concentration would be compared against the measured benzene concentration in product water to provide insight into whether this is a suitable predictive method. Since a wide range of temperature and humidity test conditions were desired to imitate conditions in which CWFA technology may be utilized (indoor and outdoor environments), the first test was verification of the AquaBoy operation in different relative humidity and temperature conditions. The second test was to determine the steady state rate of benzene in the environmental chamber while the CWFA system was in operation. The last two pilot tests were sample size determination runs to determine the variation in the methods (Table 8).

Henry's Law Projections

By applying K_H to different ambient air values of benzene found in polluted outdoor (50 µg/m^3) and indoor industrial (640 µg/m^3) environments the concentration of benzene in product and control water was calculated. This study used the EPA site assessment calculator for the Office of Solid Waste and Emergency Response (OSWER) Method to determine the temperature adjusted K_H for benzene (48). Humidity influence on the product water was addressed through temperature saturation values using experimental air temperatures (15.5, 25, 35˚C). Saturation temperature values given the relative humidity and air temperature values of each test condition are presented in Table 9. Next, this study used Henry's Law equation (EQ #2) to calculate the control and product water expected values given a targeted air concentration of benzene. Values calculated using Equation 2 with the given benzene vapor concentration and temperature are presented in Table 10 (50 µg/m^3) and Table 11 (640 µg/m^3). The lowest temperatures had the highest concentrations of benzene projected for water. All of the polluted outdoor (50 µg/m^3) levels were calculated to meet the EPA drinking water MCL standard for benzene. However, three of the lowest calculated saturation temperatures for an indoor industrial environment (640 µg/m^3) exceeded the EPA drinking water MCL standard for benzene.

$$[gas] = K_H (Pg) \qquad [EQ \#2]$$

Table 9. Saturation Temperature Values from Ambient Air Temperature Values with Relative Humidity

Ambient Air Temperature (C˚)	Relative Humidity (%)	Saturation Temperature (˚C)	K_H (atm-m^3/mol)	K_H (mol/atm-L)
15.5	45	3	0.00181	0.553
15.5	65	8	0.00239	0.418
25	45	12	0.00295	0.339
25	65	18	0.00399	0.251
35	45	21	0.00461	0.217
35	65	28	0.00636	0.157

Table 10. Henry's Law Calculated Values for Benzene Concentration in Water at 50 (µg/m^3) Benzene Vapor Concentration.

Temperature (C˚)	K_H mol/atm-L	Partial Pressure (atm)	Benzene Concentration in the Water (µg/L)
3	0.553	1.450×10^{-7}	6.26×10^{-1}
8	0.418	1.479×10^{-8}	4.70×10^{-1}
12	0.339	1.498×10^{-8}	3.97×10^{-1}
18	0.251	1.529×10^{-8}	2.99×10^{-1}
21	0.217	1.545×10^{-8}	2.62×10^{-1}
28	0.157	1.582×10^{-8}	1.94×10^{-1}
15.5	0.283	1.517×10^{-8}	3.36×10^{-1}
25	0.179	1.566×10^{-8}	2.20×10^{-1}
35	0.116	1.618×10^{-8}	1.47×10^{-1}
Light Blue: Air Temperature Values Light Grey: Saturation Temperature Values *Note: All values are within the EPA MCL for benzene (5 µg/L)			

Table 11. Henry's Law Calculated Values for Benzene Concentration in Water at 640 (µg/m^3) Benzene Vapor Concentration.

Temperature (C˚)	K_H mol/atm-L	Partial Pressure (atm)	Benzene Concentration in the Water (µg/L)
3	0.553	1.857x10^{-7}	8.01
8	0.418	1.894x10^{-7}	6.01
12	0.339	1.917x10^{-7}	5.08
18	0.251	1.957x10^{-7}	3.83
21	0.217	1.978x10^{-7}	3.35
28	0.157	2.025x10^{-7}	2.94
15.5	0.283	1.940x10^{-7}	4.30
25	0.179	2.005.x10^{-7}	2.82
35	0.116	2.072x10^{-7}	1.88

Light Blue: Air Temperature Values
Light Grey: Saturation Temperature Values
Red: Indicates values exceeding the EPA MCL for benzene (5 µg/L)

Test 1, 2, 3 &4

Test # 1 was performed to verify the manufacturer temperature performance specifications for the AquaBoy™ system and identify environmental chamber relative humidity limitations. To determine the outer limits of both temperature and relative humidity ranges for the subsequent pilot runs, five temperatures (15.5, 21.1, 25, 30, 35˚C) and five relative humidities (RH) of (35, 40, 45, 65, 90%) were tested with the AquaBoy™ system in the environmental chamber. The lowest temperature tested (15.5˚C) was the manufacturer provided minimum operating temperature for the AquaBoy™ while the highest temperature was determined during testing. To accomplish this test, the AquaBoy™ was placed into the center of the environmental test chamber. The chamber temperature and relative humidity set points (as described in Table 12) were input into the automated environmental chamber control panel. A summary of Test #1 data is provided in Table 12. The lowest temperature and relative humidity at which the AquaBoy™ system could produce water was determined to be 25˚C at 45% RH, with temperature as the limiting condition. The evaporator coils froze at temperatures below this set point. The highest temperature and relative humidity at which the AquaBoy™ system could operate was determined to be 35˚C at 65% RH. While the AquaBoy™ continued to produce water at temperatures above 35˚C, the control panel indicated a high temperature error warning above this set point. The environmental test chamber was limited to achieving RH parameters between 40-80%, with the most stable RH zone between 45-50% (± 5%). As a result of this test, a temperature of 25˚C and relative humidity of 65% were selected as the pilot run experimental conditions as the lowest achievable temperature with the highest achievable relative humidity with acceptable variation.

Table 12. Test #1 - Verification of AquaBoy and Environmental Chamber Temperature and RH parameters

Sample	Temperature (˚C)	Relative Humidity (%)	Limitation
1	15.5	45	AquaBoy evaporator coils froze
2	15.5	65	AquaBoy evaporator coils froze
3	21.1	45	AquaBoy evaporator coils froze
4	21.1	65	AquaBoy evaporator coils froze
	25	35	Chamber cannot achieve RH below 40%
5	25	45	None
6	25	65	Chamber has > ± 5% RH fluctuation
7	25	90	Chamber cannot reach above 80% RH
7	30	45	None
8	30	65	Chamber has a > ± 5% RH fluctuation
8	35	45	None
9	35	65	Chamber has a > ± 5% RH fluctuation
10	> 35	45	AquaBoy went into error mode for high temperature

Test 2 of the pilot phase was the steady state test. It was unknown how the AquaBoy system would impact the rate of benzene addition required for the environmental chamber or if the equipment on hand would produce stable conditions at a low benzene vapor concentration in the chamber. Therefore, the purpose of the steady state test was to determine the rate of benzene needed to achieve a steady state of (50 µg/m^3) in the environmental chamber with the AquaBoy system running. Results of Test 2 indicated that the rate of benzene needed to achieve 50 µg/m^3 at 25˚C and RH of 65% was between 14-10 cc/min. It was observed that the rate of benzene required to reach the target concentration declined throughout the test. It was also observed that when the CWFA system went into standby mode the fan halted and water production was suspended. Standby mode typically lasted 5 mins (± 3 mins). While in standby mode the system was not exhausting hot air and as a result the temperature in the chamber dropped a full degree. Therefore it was important to monitor standby mode occurrence and adjust the temperature in the chamber to maintain target conditions.

The purpose of Test 3 and 4 of the pilot phase was to determine variation in the experimental method and determine an appropriate sample size for the full scale tests. For these tests, the temperature and relative humidity of the environmental chamber was maintained at 25 ± 0.5 ˚C and 65 ± 7%. Benzene concentration was targeted using two, GrayWolf (AdvanceSense®) photoionization detectors (PID) with parts per billion (PPB) probes (TG - 502) as a real-time, direct-reading instrument to indicate when the target benzene concentration was reached as well as maintain a steady state benzene concentration in the chamber. Prior to the start of each test, the correction factor (0.5) for benzene was applied to the PID. A mass flow controller governed the rate of benzene addition to the chamber with the PID as a guide. The PIDs recorded benzene concentration (ppb) every 30 seconds during every one hour discrete sampling round. The baseline level of total volatile organic compound (TVOC) was recorded prior to test and the target concentration of benzene (50 µg/m^3) was added to the baseline level of TVOC. The baseline reading plus 50 µg/m^3 was the target benzene concentration for each sample. Both PIDs were calibrated every three days and bump checked daily with high and low calibration point to ensure they were within ± 5%. The high calibration point was certified gas standard 10 ppm and the low calibration point was hood air. One PID was placed next to the air intake of the CWFA system. The second PID was placed on the opposite side of the environmental chamber to evaluate distribution of benzene in the chamber.

Each test day, both the control and product water beakers were baked at a temperature of 121˚C for 5 mins before placing them into the environmental chamber.   The product water beaker was placed below the evaporator coils of the CWFA system. The control beaker containing 300 ml of deionized water was placed beside the CWFA system. Upon experiment set-up, the environmental chamber and CWFA system were stabilized for at least 20 mins prior to the start of test to permit temperature and RH to stabilize.   Product water that had accumulated during chamber stabilization period was discarded into a closed plastic container inside the environmental chamber so that only product water produced during the hour sampling time would be collected. The product water beaker was completely emptied after each 1 hour sample and replaced below the evaporator coil for the next sample. The control was completely emptied and refilled with deionized water for the next sample. Figure 6 displays the set-up for test 3 & 4.

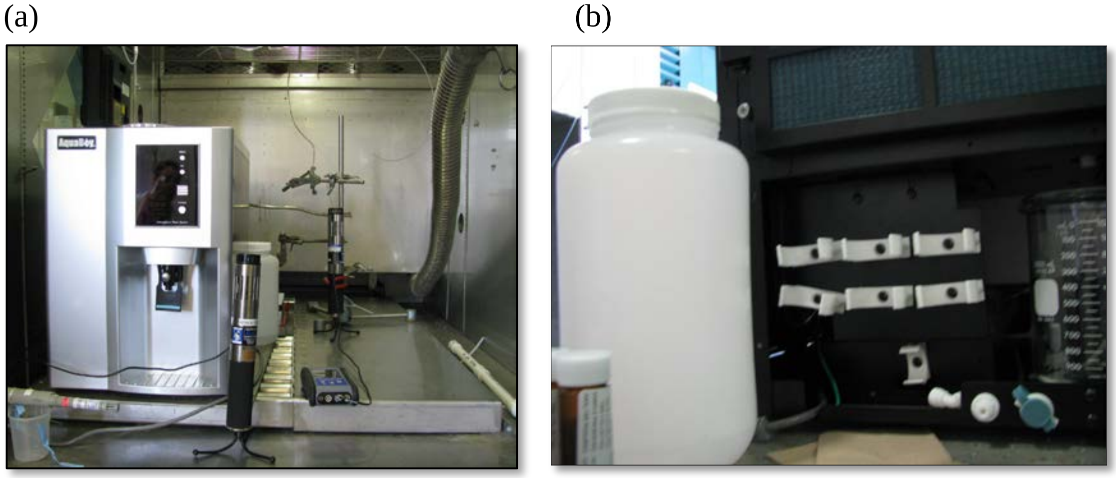

Figure 6. Pilot Test Set-up. Pilot environmental chamber experimental set-up (a). Set-up of the CWFA system from the rear view and product water collection (b).

An anomaly occurred on the third (4th sample), fourth (6th sample) and fifth day (no samples taken) of Pilot 3. On the fifth day of testing, the anomaly halted testing before the testing day began. During the chamber stabilization period, without the CWFA system turned on, the PIDs both had zero ppb readings. Only when the CWFA system was turned on to stabilize with the environmental chamber did the PIDs start to read higher than expected levels of TVOCs. The last time benzene was added to the chamber was the previous day at approximately 1500 hours. The benzene levels of the PID read approximately 30 ppb (96 $\mu g/m^3$) benzene – isobutylene equivalents, exceeding the target concentration of benzene (50 $\mu g/m^3$) and preventing further testing until the TVOC units returned to baseline. In order to speed up the sampling process for Test 4, at the start of test day the environmental chamber was heated to 49˚C for ten minutes. This temperature was chosen as the maximum temperature that would not damage the CWFA system while still driving vaporization of benzene from the CWFA system and environmental chamber. Once this step was added to the procedure, no further anomalies were experienced. The most likely explanation for the anomaly is that benzene was collecting on the condenser fins that sit behind that evaporator coils of the CWFA system.

The Full Scale Phase

The full scale phase followed the same methodology as the pilot with a few improved procedures and expanded experimental conditions. The full scale phase testing plan is outlined in Table 8. At the conclusion of the pilot phase it was clear that RH levels in the chamber above 50% had variation greater than ± 5%. Additionally, the AquaBoy™ had temperature limitations outside the range of 25 - 35˚C that would limit the test conditions for the full scale phase. Coupled with the calculation of the computed mean difference of the sample size number and the anomaly during Pilot Test 3, the full scale phase test conditions were established to ensure an adequate sample size and explore the effect of different temperatures and benzene concentrations in the air on the product water of the CWFA system. The full scale phase consisted of 24 discrete one hour sampling rounds that were split into four separate test conditions with each test condition consisting of six discrete one hour sample rounds. Testing for each condition took place over a period of 2 – 3 days.

Sample Size Determination

Statistical power and sample size calculations were determined using pilot data and the POWER procedure in the statistical analysis software (SAS) program version 9.3 for Windows. Table 13 displays the mean and standard deviation from the 12 control and product water samples of the pilot phase. Using the pooled standard deviation, a power calculation was determined assuming that the data would be analyzed using a t-test with a 5%, two-sided significance level. The power required was set at 80% to detect differences between the temperature and relative humidity groups (for the pilot phase – for the full scale phase RH was kept stable and benzene concentration was varied per test). Table 14 provides the smallest difference that could be detected between the groups at a certain sample size given an 80% power. Given the power analysis calculation, calculated Henry's Law water data was used to predict the amount of benzene that would be present in the water using the pilot phase average benzene concentration in the air (250 $\mu g/m^3$) with low and high temperature values along with low, medium, and high RH values. Calculated Henry's Law water data given benzene concentration in air, temperature and RH data is shown in Table 15. This analysis determined that a sample size of six, detecting a difference between the means of 359 ng/L, would be adequate with the exception of the saturation temperatures of 18˚C to 20˚C and 28˚C to 30˚C. Using a sample size of six, it would be difficult to detect a difference between 65 and 75% RH. Since relative humidity was determined to have > ± 5% at RH above 50% in the pilot phase, it was decided to maintain RH at steady state of 45 (± 5%) during the full scale phase in order to limit variation in the experiment.

Table 13. Pilot Phase Mean and Standard Deviation Data.

Parameter	**Control Water (ng/L)**	**Product Water (ng/L)**
Mean	626.67	2725
Standard Deviation	157.45	297.56
Pooled Standard Deviation	227.50	

Table 14. Power Analysis Calculation at 80% Power and 5% Significance.

Computed Mean Difference	
Samples Per Group	Mean Difference Detected
4	476
5	405
6	359
7	326
8	301

Table 15. Henry's Law Calculations for Benzene Concentration in the Water with a 250 µg/m^3 Benzene Concentration in the Air

Temperature (Celsius)	**Calculated Benzene Concentration in Water (ng/L)**
25	1100
35	736
12 (25˚C/45RH)	1980
18 (25˚C/65RH)	1500
20 (25˚C/75RH)	1370
21 (35˚C/45RH)	1300
28 (35˚C/65RH)	971
30 (35˚C/75RH)	884
Light Blue: Air Temperature Values Light Grey: Saturation Temperature Values	

Conditions 1-4

The full scale phase was run in a different environmental chamber from the pilot phase. At the time of the full scale testing, indoor painting operations in the building containing the pilot chamber laboratory impacted the air quality with low levels of VOCs. Due to the presence of these paint-related VOCs in the air, the PID did not reflect the benzene concentration in the chamber of the pilot environmental chamber, requiring the use of a different chamber in another building. Figures 7 shows the set-up of the full scale phase tests in the new chamber. Temperature was tested at a low (25 ± 0.3˚C) and high (35 ± 0.3˚C) value and relative humidity was kept constant (45 ± 5%). High (640 µg/m^3) and low (50 µg/m^3) concentrations of benzene were targeted using two PIDs consistent with the methods of pilot 3 & 4. One PID was placed next to the air intake of the CWFA system. The second PID was placed on the opposite side of the environmental chamber to evaluate distribution of benzene in the chamber. A mass flow controller governed the rate of benzene addition to the chamber with the PID as a guide. Table

16 shows the average rate of benzene added to the chamber per test condition. Both PID air monitors were calibrated at the start of every new test condition with the exception of test condition 2. One meter was calibrated at the start of the test condition and the second meter was calibrated before discrete sampling round number 4. The high calibration point was certified gas standard 7.5 ppm (BuyCalGas, Conyers, GA) and low calibration point was Zero air, certified gas standard (BuyCalGas, Conyers, GA).

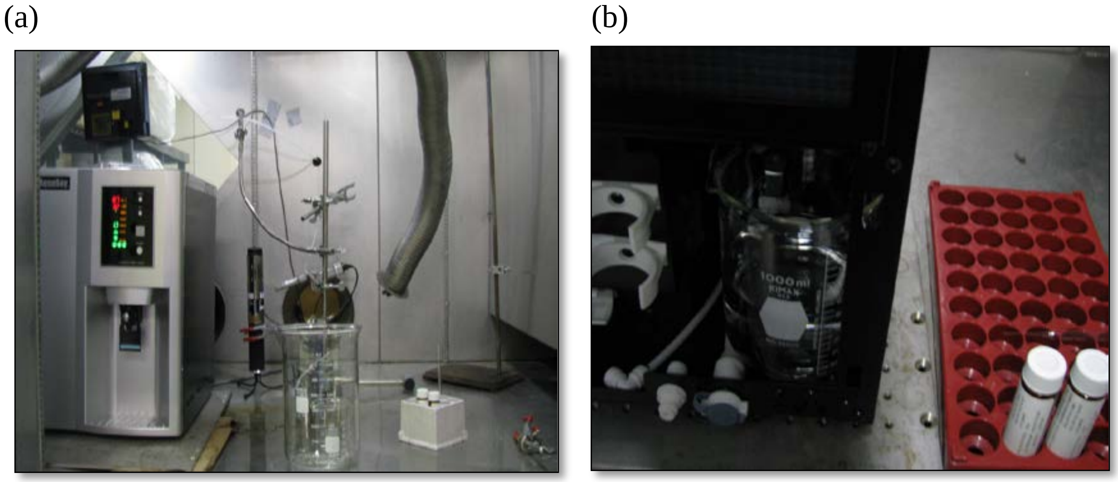

Figure 7. Full Scale Set-up. Full scale environmental chamber experimental set-up (a). Set-up of the system from the rear view and product water collection (b).

Based on lessons learned from the pilot scale tests, the chamber was set at 49˚C for 15 minutes prior to the start of the test each day to volatilize and exhaust excess benzene from the chamber and CWFA system. Additionally, both the control and product water beakers were baked at a temperature of 121˚C for 15 mins before placing them into the environmental chamber. The control beaker containing 300 mL of deionized water was placed into a 1L beaker to mimic conditions of the product water beaker. The remaining full scale procedures followed pilot phase methods.

Table 16. Average Mass Flow Controller Setting per Test.

Test	Flow Rate of Benzene into Chamber to Reach Saturation (cc/min)	Average Flow Rate of Benzene into Chamber (cc/min)
Condition 1	8	5.44
Condition 2	9	5.69
Condition 3	45	38.84
Condition 4	48	41.31

Post Full Scale Test

Two additional product water samples were taken at the end of the full scale test to evaluate the repeatability of the experiment with a different type of air filter. The purpose of this additional test was to determine if a different type of air filter would impact the product water quality of the CWFA system. For this test, the temperature and RH of the environmental chamber was maintained at 25 ± 0.3 ˚C and 45 ± 5%, with a target concentration of 640 $\mu g/m^3$ to mimic experimental condition 3 of the full scale test. A manufacturer provided replacement air filter was used for the post full scale test. The replacement air filter was a high capacity minimum efficiency reporting value (MERV) of 11. The original electrostatic air filter uses metal wire mesh to attract smaller dust particles which was absent from the MERV 11 filter. Both filters are pictured in Figure 8. Only product water was collected for this test. All other experimental procedures followed the full scale phase protocols.

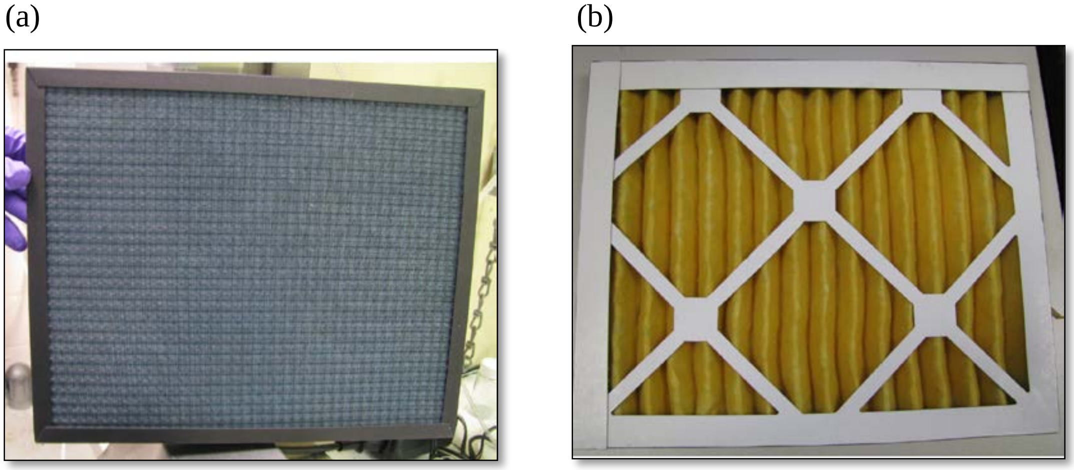

Figure 8. Original Electrostatic Air Filter (a) Replacement MERV 11 Air Filter (b)

DATA COLLECTION AND ANALYTICAL METHODS

Air and water samples were collected and analyzed for benzene. Air samples consisted of direct and indirect sampling with a PID and summa canister air samples. Water samples consisted of a product and control sample. The control water was placed under the same conditions as the product water and used as a comparison for calculated and product water benzene concentrations.

Air Data Collection

In addition to direct benzene air monitoring, indirect benzene samples were collected into 6.0 liter (L) pre-cleaned and pre-evacuated summa canisters (Restek) during each discrete sampling round. The summa canister was connected to 50.8 mm of 6.35 mm inner diameter (ID) x 9.53 mm OD Tygon tubing that connected to 0.6 m of 3.18 mm OD Teflon tubing which was routed through the sampling port hole into the environmental chamber. The summa canister air sample was collected within six inches of the air intake of the CWFA system. During pilot 3 & 4, a 30 second grab summa canister sample was collected every other sample. During full scale testing, five of the six discrete air samples collected per condition consisted of 30 second grab samples with the remaining discrete air sample collected over the one hour sampling period. The critical orifice was removed from the summa canister to facilitate a 30 second grab sample of 6.0 L. The one hour sample was collected at a flow rate of 70 milliliters (ml)/min. The purpose of the hour long sample per test condition was to verify the reliability of the 30 sec grab samples. Summa canisters were analyzed by laboratory analysis using U.S. EPA method TO-15 with gas-chromatography-mass spectrometry (GC-MS) (43). All quality control for the laboratory analysis of the samples were within specifications. The mean coefficient of variance between duplicate summa canister grab samples was 16 ± 14%. Field duplicate samples were taken consecutively rather than simultaneously, and so the variation in duplicate samples maybe the result of a high rate of air exchanges in the chamber.

Water Data Collection

Water samples were collected in two 1000 mL (pilot) and 400 mL (full scale) glass beakers. The glass beakers were washed in laboratory detergent (Alconox Powder) and rinsed with tap water at the start of every test day. The control beaker contained 300 mL of deionized water that was open to the atmosphere in the same matter as the product water beaker and remained in the chamber throughout the one hour sampling period. At the end of the one hour sample period, water samples were collected utilizing the chamber hand inserts to transfer water into 40ml glass vials with Teflon® septa. Water samples were analyzed for benzene every sample round (24 samples) while samples analyzed for total organic carbon (TOC) were analyzed every other sample round (12 samples). The 40 ml sample glass vials to be analyzed for benzene were prepared with a 1:1 hydrochloric acid solution in order to lower the pH ≤ 2 and preserve the sample. The 40 ml glass vial to be analyzed for TOC were prepared with a 1:1

sulfuric acid solution in order to lower the pH ≤ 2 and preserve the sample. The 40 ml glass vials were filled in a manner to minimize agitation and completely filled to avoid any headspace. After sampling was complete the 40 ml sample TOC and benzene vials were placed into a portable freezer kept between 0 – 4˚C for transport the laboratory for analysis. All samples were analyzed within 14 days.

Sampling Plan

Air and water sampling was comprised of one hour sampling events for both the pilot and full scale phases. The pilot phase was comprised of 12, one hour sampling events detailed in Table 17. The full scale phase consisted of 24 discrete one hour sampling rounds that were split into four separate test condition. Each condition consisting of six discrete one hour sample rounds. The full scale sampling scheme is detailed in Table 18. Background levels of benzene in the control and product water were recorded at the start of the pilot and full scale phases. Background levels of benzene in the chamber air were sampled at the start of the full scale phase.

Table 17. Number and Type of Samples Collected for the Pilot Test.

Pilot Test 3 & 4	Baseline	Method 524.2 SIM (Benzene)	Method 415.3 (TOC)	Method TO-15 Grab Air Samples
Control Water	1	12 1 Duplicate 1 Field Blank	6	
Product Water	1	12 1 Duplicate 1 Field Blank	6	
Summa Canister	1			6

Table 18. Number and Type of Samples Collected for the Full Scale Test.

Test Conditions 1 - 4	Base-line	Method 524.2 SIM (Benzene)	Method 415.3 (TOC)	Method TO-15 Grab Air Samples	Method TO-15 1 hr Air Sample
Control Water	1	24 4 Duplicates 4 Blanks	12		
Product Water	1	24 4 Duplicates 4 Blanks	12		
Summa Canister	1			20 4 Duplicate	4

DATA PROCESSING AND ANALYSIS

The Shapiro Wilk Test was run to determine if the data followed a normal distribution. In this test a non-significant result ($p>0.05$) equals a normal distribution. A t-test was used to determine if there was a statistical difference between the means of the product and control water samples at different benzene air concentrations and between the means of benzene concentrations of the product and control water samples at different temperatures. Equation 4 was applied to normalize benzene vapor concentrations in order to evaluate the benzene concentration in the product water due to variations in air concentrations between sampling iterations with the same target concentration. Air data normalization assumes the linear relationship that Henry's Law denotes. Additionally, different benzene vapor concentrations were normalized to eliminate the influence of a fluctuating benzene air concentration per sample.

$$Tw = \frac{W}{A} \times \ t_c \qquad \text{[EQ \#4]}$$

In which:

Tw = Benzene product water concentration at target benzene air concentration (µg/L)

W = Mean concentration of benzene in product water per test (µg/L)

A = Mean air concentration per test (µg/m^3)

t_c = Target benzene air concentration per test (µg/m^3)

CHAPTER 3: RESULTS AND DISCUSSION

This chapter is a manuscript that is being submitted to the peer-reviewed journal *Science of the Total Environment*

INTRODUCTION

Globally, available drinking water resources are diminishing in both quantity and quality. Growing concerns about water scarcity and drinking water shortages have renewed interest in alternate methods of obtaining water, which includes, Water From Air (WFA) technology. This technology is currently applied to create water from atmospheric moisture in military, commercial, industrial, and residential applications. The United States (U.S.) Army is interested in WFA technology to improve logistical efficiencies in water production, purification, and distribution to reduce reliance on intermediate staging bases and sustainment logistics. The ideal WFA technology envisioned would improve the U.S. military's ability to conduct military operations by bringing water production and purification closer to the point of need and thereby improve unit self-sufficiency (2). The WFA technology has the potential to be used worldwide in outdoor and indoor environments. Of the outdoor environments, megacities may be the most significant. Megacities are dense urban environments comprised of populations greater than 10 million. Since sixty percent of the world's population is projected to live in urban environments by 2030, it is likely that future U.S. military operations may occur in areas that are congested and highly polluted (9). Since megacities are mostly emerging in low-income countries in which drinking water resources may be inadequate, WFA technology may become an appealing possibility to local governments and nongovernment organizations for residential and commercial applications. WFA technology applications in indoor setting are also important because indoor air quality has the potential to be extremely poor. In a military deployment setting, personnel conduct refueling operations, automotive repair, weapons cleaning, and painting operations in indoor and outdoor settings. When conducted indoors, these military operations as well as other similar non-military industrial processes can lead to extremely poor air quality. Currently, there are limited guidelines or special considerations for the prolonged operation and maintenance of the WFA water treatment systems in indoor industrial or polluted outdoor settings. Thus, it is important to characterize the water quality of drinking water produced from WFA technology when used in highly polluted environments.

Water From Air Technology

The WFA systems extract water from the air for both potable and non-potable purposes. The WFA technology concept is not new, with condensation WFA feasibility experiments dating back more than 45 years (12). However, given the high energy requirement to capture water from the air, it is a technology that is most attractive in situations in which water is expensive to procure or not readily available. Given growing global concerns about water scarcity and drinking water shortages, interest in this technology has grown. The two most common types of WFA systems utilize either condensation or desiccant technology. Condensation Water From Air (CWFA) systems operate by condensing water vapor to form liquid droplets. CWFA systems accomplish the phase change from a vapor to liquid by cooling air to the saturation temperature. Often the saturation temperature is lower than the ambient air temperature. The compressor, condenser, evaporator, and a liquid medium in the CWFA systems are the primary components essential to the vapor compression cycle and process air flow that drive the cooling process for the CWFA system, which is very similar to an in-home dehumidifier. It is important to note that not all condensate systems are the same. Condensate systems vary in design for improvements in energy efficiency and water treatment. Nevertheless, the core process is very similar in most condensation technologies.

In the United States, CWFA system product water intended for drinking water purposes must meet the EPA drinking water standards. Furthermore, in a military deployed setting, CWFA system product water must meet the military tri-service Long Term Potability (LTP) standards for military field drinking water, found in Army Technical Bulletin Medical (TB MED) 577 (2010). However, there is currently little data available to determine the relationship between air contaminants and the rate at which they are transferred from the air into CWFA product water. As a result, there is uncertainty regarding the appropriate level and maintenance interval of water treatment modules to ensure CWFA systems meet the EPA drinking water standards given such a wide array of potential environments with different and fluctuating air quality compositions. Walhgren's (53) review on WFA technology indicated that water produced from the atmosphere may not be safe to drink without treatment. Gandhiasan and Abualhamayel (10) specified that in polluted urban and industrial environments, water quality of desiccant WFA systems may be compromised and should be monitored. Previous studies have tested the water quality of WFA systems, but no studies have quantified the relationship of air quality data and its impact on WFA product water quality (6, 10, 37, 53). Thus, there is a need for research to investigate how quantified amounts of volatile organic compounds (VOC) in the air will affect the product water quality of CWFA systems.

Benzene (C_6H_6) was selected as the VOC contaminant of concern for this study primarily because of its physical characteristics, likelihood of presence in both indoor industrial and outdoor urban environments, and potential adverse health effects. Benzene is a colorless aromatic liquid at room temperature, but evaporates quickly into the atmosphere and is present at low levels in the ambient air around the world (1). The most severe health effect of benzene exposure is death, which has been documented to occur at high oral doses. However, benzene's most well-known and significant toxic property is that it is a carcinogen. Acute non-lymphocytic leukemia has been causally associated with chronic occupational inhalation exposures to benzene. While there are no human studies that have investigated the potential for carcinogenicity due to benzene ingestion, there have been several animal studies that have found evidence of benzene acting as a multiple site carcinogen (13, 18).

This study investigated the effects of benzene air concentrations, representative of both polluted outdoor urban and indoor industrial environments, on the concentration of benzene in untreated product water from a CWFA system. Specific objectives were to: (1) investigate the relationship of benzene air concentration and temperature with the concentration of benzene in untreated product water, (2) compare water quality results to military and U.S. EPA drinking water standards (40, 46), (3) inform health risk assessments and selection of appropriate level and lifespan of water treatment for future WFA technologies to minimize exposure to benzene contamination from ingestion.

MATERIALS AND METHODS

Experimental Set-up

A small scale, commercially available CWFA system for use in residential or office buildings was selected to generate water for untreated product water tests. In order to evaluate strictly the untreated product water, the CWFA system water treatment module was removed from the system. A calibrated Dickson thermocouple temperature logger (Model KT802) was secured to the outer evaporator coil in the CWFA system in order to monitor and track coil temperature. An environmental chamber was utilized to maintain benzene, temperature, and relative humidity at steady state conditions. Figure 9 shows a schematic diagram of the environmental chamber set-up. The environmental chamber measured 2.56 m x 1.07 m x 1.20 m with a total volume of 3.13 m^3, adjusted for equipment in the chamber. The chamber had multiple access points including one sampling port door, one sample port hole, a main door, and two sets of hand inserts (one on each side). The chamber was supplied with unfiltered indoor air at a flow rate of 81 air changes per hour (ACH). Due to the nature of the chamber design, the ACH rate was not operator controlled. Relative humidity in the chamber was automated and controlled by dehumidification coils and a water vapor generator. The tap water used to generate humidity was filtered through a carbon filter to remove organic impurities prior to entering the chamber. Temperature in the chamber was also automated and controlled by refrigeration and nichrome heating elements. A calibrated Vaisala HUMICAP® hand held humidity and temperature meter (model number HM141) was placed inside the chamber to track and monitor relative humidity and temperature readings during the test to verify they were within the target ranges.

Benzene, contained in a certified compressed gas cylinder containing 0.322 m^3 of 1.01 MOLE % concentration benzene (HP GAS LLC), was introduced into the chamber at a pressure of 1.266 kilograms per square centimeter and a rate controlled by a calibrated, Seirra, mass flow controller (Smart-trak®, 10-50 cubic centimeter (cc) /minute (min)). The cylinder was connected to a mass flow controller by 3.18 mm outer diameter (OD) straight Teflon tubing with 3.18 mm Swagelok tube fittings. Additional Teflon tubing was routed from the mass flow controller through the sample port door of the chamber. Inside the chamber, a six way Teflon tubing network was mounted evenly across the ceiling of the chamber in order to uniformly distribute benzene within the chamber.

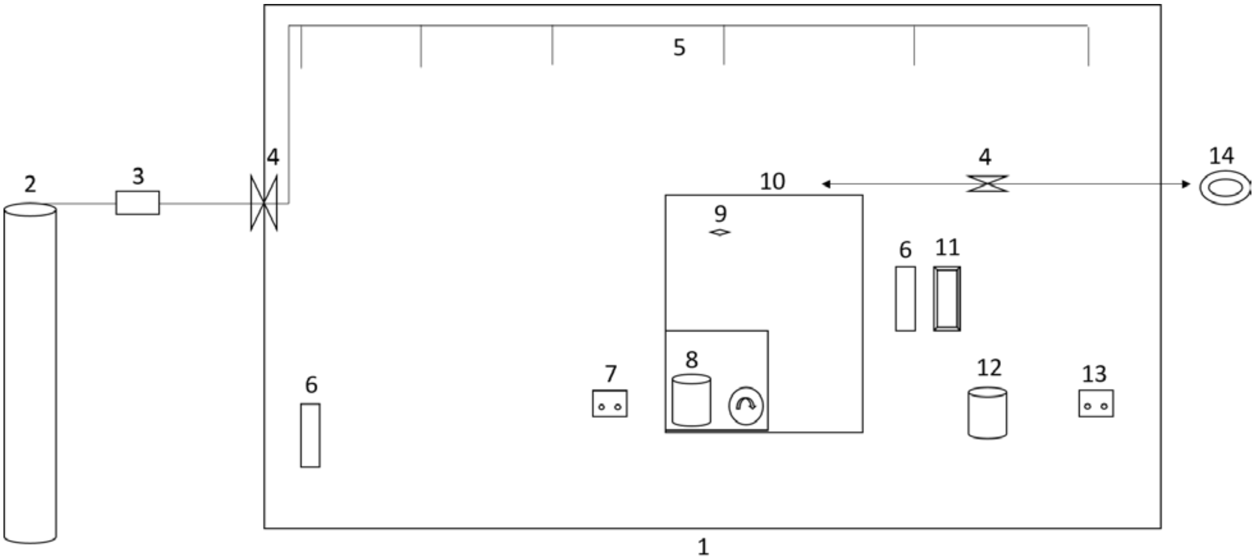

Figure 9. Schematic Diagram of the Full Scale Environmental Chamber. 1. Environmental chamber, 2. Benzene gas cylinder, 3. Mass flow controller, 4. Chamber access point, 5. Teflon tubing network, 6. PPB PIDs, 7. Product water collection vials, 8. Product water collection beaker, 9. Thermocouple, 10. CWFA system, 11. Humidity and temperature meter, 12. Control water beaker, 13. Control water collection vials, 14. Summa canister

Experimental Procedure

This study was conducted in two phases: the pilot and full scale. The primary purpose of the pilot test was to determine variation in the experimental method and calculate an appropriate sample size for the full scale test. Additionally, the pilot test was used to implement a new experimental method to test the product water of CWFA system in known benzene vapor concentrations. The full scale test implemented improved experimental procedures learned during the pilot test and expanded upon the experimental test conditions. Air and water samples were collected during discrete one hour sampling rounds and analyzed for benzene. A summary of pilot and full scale tests are in Table 19.

Table 19. Summary of Pilot and Full Scale Tests

Test	**Type of Test**	**Benzene Concentration ($\mu g/m^3$)**	**Temperature (°C)**	**Relative Humidity (%)**	**Discrete 1 hr Sampling Rounds**
Pilot 1	Verification of temperature and RH	None	15.5 - 35	45 - 90	NA
Pilot 2	Steady state Test	50	25, 35	45, 65	NA
Pilot 3	Sample Size Determination	50	25	65	6
Pilot 4	Sample Size Determination	50	25	65	6
Condition 1	Full Scale	50	25	45	6
Condition 2			35		6
Condition 3		640	25		6
Condition 4			35		6

The Pilot Phase

This study implemented a new experimental method to test the product water of a CWFA system at known benzene air concentrations in an environmental chamber. The pilot phase consisted of Henry's Law calculations and four separate pilot tests in the environmental chamber (See Table 19). Based on pilot study experiments it was determined to conduct the full scale testing using two temperatures (25˚C and 35˚C), 45% RH, and two different benzene concentrations representing polluted outdoor and an indoor industrial environment. Henry's Law states at a constant temperature, the amount of gas that is dissolved in a solvent is directly proportional to the partial pressure of that gas and concentration in the water (7). Therefore, a temperature-adjusted Henry's Law constant can be applied in Henry's Law Equation 2 to calculate the amount of benzene concentration in the product water (19):

$$[gas] = K_H (Pg) \qquad \text{[EQ \#2]}$$

In which:

$[gas]$ = moles of gas per liter of solution (mol/L)

K_H = Henry's Law constant (mol/L*atm)

Pg = Partial pressure of the gas (atm) above the solution

Temperature adjusted K_H for benzene were determined from the EPA site assessment calculator applying the Office of Solid Waste and Emergency Response (OSWER) Method (48). Henry's Law calculations were used to determine the theoretical benzene concentration in control and product water given a target concentration of benzene in the air. Given the wide array of benzene concentrations found in the literature, this study targeted 50 $\mu g/m^3$ as a representative global average benzene level for a polluted outdoor urban environment (5, 14, 15, 21, 24, 35, 54). Likewise, given the wide range of indoor industrial benzene levels for the designated operations, this study targeted 640 $\mu g/m^3$ to represent a contaminated indoor industrial setting (8, 34, 52).

The Full Scale Phase

The full scale phase was informed by the pilot phase with a few improved procedures and expanded experimental conditions. The full scale phase consisted of 24 discrete one hour sampling rounds that were split into four separate test conditions with each test condition consisting of six discrete one hour sample rounds. Testing for each condition took place over a period of 2 – 3 days. Power and sample size calculations were determined using pilot data and the POWER procedure in the statistical analysis software (SAS) program version 9.3 for

Windows. Figures 9 and 10 show the set-up of the full scale phase tests in the environmental chamber. Temperature was tested at two conditions, a low (25 ± 0.3˚C) and high (35 ± 0.3˚C) value while relative humidity was kept constant (45 ± 5%). High (640 µg/m^3) and low (50 µg/m^3) concentrations of benzene were targeted using two, GrayWolf (AdvanceSense®) photoionization detectors (PID) with parts per billion (PPB) probes (TG - 502) as a real-time, direct-reading instrument to indicate when the target benzene concentration was reached as well as to maintain a steady state of benzene concentration in the chamber. Prior to the start of each test, the correction factor (0.5) for benzene was applied to the PID. A mass flow controller governed the rate of benzene addition to the chamber with the PID as a guide. The PIDs recorded benzene concentration (ppb) every 30 seconds during every one hour discrete sampling round. Both PID air monitors were calibrated at the start of every new test condition with the exception of test condition 2. One meter was calibrated at the start of the test condition and the second meter was calibrated before discrete sampling round number 4. The high calibration point was certified gas standard 7.5 ppm (BuyCalGas, Conyers, GA) and low calibration point was Zero air, certified gas standard (BuyCalGas, Conyers, GA). One PID was placed next to the air intake of the CWFA system. The second PID was placed on the opposite side of the environmental chamber to evaluate distribution of benzene in the chamber.

Figure 10. Environmental Chamber Set-up (2). Water from air system (left), control water (center) and benzene sampling vials (right)

Prior to starting the test each day, the chamber was set at 49˚C for 15 minutes to volatilize and exhaust excess benzene from the chamber and CWFA system. Additionally, both the control and product water beakers were baked at a temperature of 121˚C for 15 mins before placing them into the environmental chamber. The control beaker containing 300 mL of deionized water was placed into a 1L beaker to mimic conditions of the product water beaker. The product water beaker was placed below the evaporator coils of the CWFA system. Upon experiment set-up, the chamber and system were stabilized for at least 20 mins prior to the start of the test to permit temperature and relative humidity levels to stabilize at test conditions. Product water that had accumulated during chamber stabilization period was discarded into a closed plastic container inside the environmental chamber so that only product water produced during the hour sampling time would be collected. The product water beaker was completely emptied after each 1 hour sample and replaced below the evaporator for the next sample. The control was completely emptied and refilled with deionized water for the next sample.

An additional run to collect two additional product water samples was conducted at the end of the full scale test to evaluate the repeatability of the experiment with a different type of CWFA system air filter. For this test, the temperature and relative humidity of the environmental chamber was maintained at 25 ± 0.3 ˚C and 45 ± 5%, to mimic experimental conditions of condition 1. The manufacturer-provided replacement filter was a high capacity minimum efficiency reporting value (MERV) of 11, whereas the original filter was an electrostatic air filter. Only product water was collected for the post-full scale experiment. All other experimental procedures followed the full scale phase protocols.

Data Collection and Analytical Methods

Air Data Collection

Apart from direct benzene air monitoring, indirect benzene samples were collected into 6.0 liter (L) pre-cleaned and pre-evacuated summa canisters (Restek) during each discrete sampling round. The summa canister was connected to 50.8 mm of 6.35 mm inner diameter (ID) x 9.53 mm OD Tygon tubing that connected to 0.6 m of 3.18 mm OD Teflon tubing which was routed through the sampling port hole into the environmental chamber. The summa canister air sample was collected within six inches of the air intake of the CWFA system. During testing, five of the six discrete air samples collected per condition consisted of 30 second grab samples with the remaining discrete air sample collected over the one hour sampling period (Table 20). The critical orifice was removed from the summa canister to facilitate a 30 second grab sample of 6.0 L. The one hour sample was collected at a flow rate of 70 milliliters (ml)/min. The purpose of the hour long sample per test condition was to verify the reliability of the 30 sec grab samples. Summa canisters were analyzed by laboratory analysis using U.S. EPA method TO-15 with gas-chromatography-mass spectrometry (GC-MS) (43). All quality control for the laboratory analysis of the samples were within specifications. The mean coefficient of variance between duplicate summa canister grab samples was 16 ± 14%. Field duplicate samples were taken consecutively rather than simultaneously, and so the variation in duplicate samples maybe the result of a high rate of air exchanges in the chamber.

Table 20. Number and Type of Samples for the Full Scale Test.

Test Conditions 1 - 4		Base-line	Method 524.2 SIM (Benzene)	Method 415.3 (TOC)	Method TO-15 Grab Air Samples	Method TO-15 1 hr Air Samples
Samples Taken	Control Water	1	24 4 Duplicates 4 Blanks	12		
	Product Water	1	24 4 Duplicates 4 Blanks	12		
	Summa Canister	1			20 4 Duplicate	4

Water Data Collection

Control and product water samples were collected in two 400 mL glass beakers. The glass beakers were washed in laboratory detergent (Alconox Powder) and rinsed with tap water at the start of every test day. The control beaker contained 300 mL of deionized water that was open to the atmosphere in the same manner as the product water beaker and remained in the chamber throughout the one hour sampling period. At the end of the one hour sample period, water samples were collected utilizing the chamber hand inserts to transfer water into 40ml glass vials with Teflon® septa. Water samples were analyzed for benzene every sample round (24 samples) while samples analyzed for and total organic carbon (TOC) were analyzed every other sample round (12 samples) (Table 20). The 40 ml sample glass vials to be analyzed for benzene were prepared with a 1:1 hydrochloric acid solution in order to lower the pH ≤ 2 and preserve the sample. The 40 ml glass vial to be analyzed for TOC were prepared with a 1:1 sulfuric acid solution in order to lower the pH ≤ 2 and preserve the sample. The 40 ml glass vials were filled in a manner to minimize agitation and completely filled to avoid any headspace. After sampling was complete the 40 ml sample TOC and benzene vials were placed into a portable freezer kept between 0 – 4˚C for transport the laboratory for analysis. All samples were analyzed within 14 days.

A contracted laboratory completed benzene and TOC analysis. Analytical procedures for the determination of benzene were based on the U.S. EPA Method 524.2 in selected ion monitoring mode (SIM) with gas-chromatography-mass spectrometry (GC-MS) (44). While analytical procedures for the determination TOC were based on EPA Method 415.3 (45). No contaminants were detected in laboratory blank samples. One of four trip blank samples had a 5.8 ng/L detection for benzene, indicating a point of minor cross contamination during laboratory processing or transport. The mean coefficient of variance between duplicate water samples was 6.7 ± 5.5%.

Data Processing and Analysis

The Shapiro Wilk Test was run to determine if the data followed a normal distribution. A t-test was used to determine if there was a statistical difference between the means of the product and control water samples at different benzene air concentrations and between the means of benzene concentrations of the product and control water samples at different temperatures. Equation 4 was applied to normalize benzene vapor concentrations with the same target concentration in order to evaluate the product water benzene concentrations due to variations in air concentrations between sampling iterations. Air data normalization assumes the linear relationship that Henry's Law denotes. Additionally, different benzene vapor concentrations were normalized to eliminate the influence of a fluctuating benzene air concentration per sample.

$$Tw = \frac{W}{A} \times t_c \qquad \text{[EQ \#4]}$$

In which:

Tw = Benzene product water concentration at target benzene air concentration (µg/L)

W = Mean concentration of benzene in product water per test (µg/L)

A = Mean air concentration per test (µg/m^3)

t_c = Target benzene air concentration per test (µg/m^3)

RESULTS AND DISCUSSION

Influence of Benzene Vapor Concentration and Temperature on Product Water

Benzene concentration in CWFA system product water, with a steady state air temperature and relative humidity, was dependent on the concentration of benzene in the air (Table 21). T-test analysis demonstrated that there is a statistically significant ($p = 0.0001$) difference between the means of benzene concentration in the product water with benzene air concentrations of 50 µg/m^3 and 640 µg/m^3. This finding is consistent with predictions based on Henry's Law; as benzene vapor concentration increases, so will the concentration of benzene in water at equilibrium. Benzene air concentrations representing a polluted outdoor environment (50 µg/m^3) at 25˚C and 35˚C (Table 21) resulted in mean product water concentrations of benzene (0.44 µg/L) that were over an order of magnitude below the USEPA and the military drinking water limit of 5µg/L (40, 46) (Figure 11). Whereas benzene air concentrations representing an indoor industrial environment (640 µg/m^3) at 25˚C and 35˚C (Table 21) resulted in product water concentrations of benzene that were 100% and 6% above the drinking water limit, respectively (Figure 11). The grab air sample coefficient of variance for test conditions 1-4 were 26, 68, 37, and 29%, due in part to the automated high ACH rate in the environmental chamber. The one hour air sample per test condition provides a more accurate representation of the benzene concentration in the air of the chamber throughout the sample period. The mean of the grab air samples per test condition provide a more accurate representation of the benzene vapor concentration, as compared to the hour long air sample per test condition. The mean of grab air samples for test conditions 1-4 were within: 14.2, 66, 6.3, and 2.4% of the one hour air sample per test condition. Low precision between grab and one hour samples for test condition 2 may have been the result of a change in the calibration zero air gas for one of PIDs prior to the start of discrete sample round 4. In order to perform the corresponding analysis, the mean of the grab and one hour air samples have been calculated for each test condition. The mean benzene vapor concentrations for test conditions 1-4 were 106, 115, 768, and 847µg/m^3.

Table 21. Temperature and Benzene Vapor Concentration Affect on Product Water from CWFA System and the Control.

Test #	Temperature (˚C)	RH (%)	Normalized Benzene Air Concentration (µg/m^3)	Mean Concentration of Benzene in the Product Water (µg/L)	Mean Concentration of Benzene in the Control Water (µg/L)
Condition 1	25	45	50	0.54 ± 0.05	0.10 ± 0.04
Condition 2	35			0.33 ± 0.03	0.05 ± 0.00
Condition 3	25		640	10.0 ± 0.53	0.79 ± 0.18
Condition 4	35			5.34 ± 0.22	0.72 ± 0.31

Results represent mean and standard devition values. Benzene vapor concentrations were normalized to the target air concentrations of 50 µg/m^3 and 640 µg/m^3

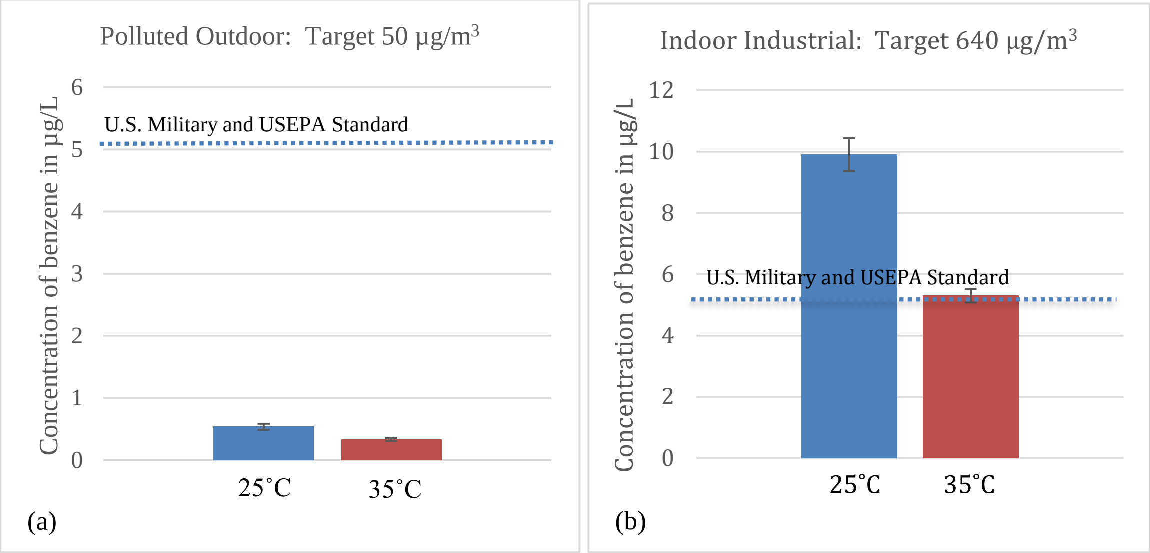

Figure 11. Benzene Concentration in the Product Water at Different Benzene Vapor Concentrations.

The mean concentration of benzene in product water at 25˚C and 35˚C given normalized benzene vapor concentrations to the target air concentration of 50 µg/m^3 (a) and 640 µg/m^3 (b). Standard deviations of the product water data are shown.

Similarly, there was a statistical difference ($p = 0.0001$) between the mean benzene concentration of product water with chamber air temperatures of 25˚C and 35˚C. The lower chamber air temperature (25˚C) had approximately double the product water benzene concentration than the higher chamber air temperature (35˚C) at the same target concentrations (Table 21). This finding is consistent with Henry's Law calculations with a temperature adjusted K_H would predict. Higher temperatures increase the potential for benzene vaporization, while lower temperatures retain more benzene in the water. Even after accounting for this difference, there was a significant increase in the measured product water benzene concentrations compared to the calculated values. Given the wide array of temperatures in which the CWFA system are operated, ambient air temperature is an important factor in benzene concentration in product water.

Untreated Product Water vs Calculated Henry's Law Values

When chamber air temperature along with benzene vapor concentration were incorporated into the Henry's Law equation, measured product water values were always greater than calculated values for benzene concentration in the product water (ranging from 2.1 to 3.8 times greater) for conditions 1-4 (Figure 12). Since water vapor from the air condenses on the evaporator coils of the CWFA system at or below the saturation temperature, the coil temperature and not ambient air temperature is most likely the controlling temperature to be applied to K_H. To evaluate this, benzene vapor concentrations and coil temperature were applied to the Henry's Law equation. The results indicate that coil temperature calculated values align closest to measured product water values. However, measured product water values also exceeded calculated coil temperature values (ranging from 1.2 – 2.1 times greater) measured in each test condition (Figure 12). Since all measured values were above calculated values, there may be factors in addition to temperature and benzene vapor concentration that contribute to the amount of benzene in product water of CWFA systems.

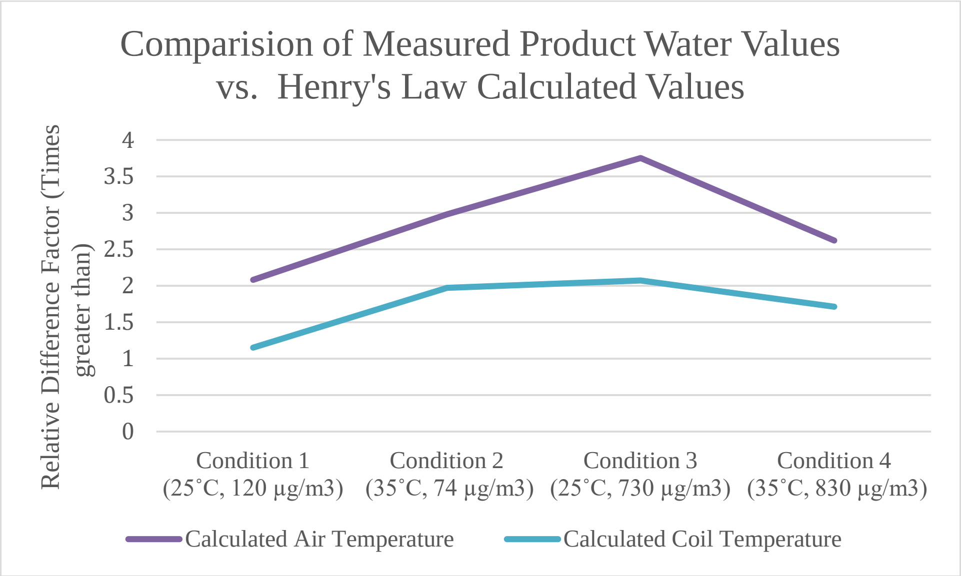

Figure 12. Comparison of Measured Product Water Values vs. Henry's Law Calculated Values. Measured product water values from the one hour air sampling period per test condition were used for this analysis. Relative difference is the ratio of the measured product water value to the calculated product water values using Henry's Law, applying both coil and air temperature. Factors closest to one indicate a closer relationship to measured product water values.

Multiple studies investigating the VOC and SVOC concentrations in dew, rain and fog have shown enrichment factors, defined as the ratio of the observed VOC and SVOC concentration in water to the calculated value, as predicted by the Henry's Law equilibrium relationship (25-27, 29, 30, 50, 51). The mechanisms for the enrichment factors in these studies include: (1) the effects of temperature correction on Henry's law constant (2) the effect of organic matter on the solubility of a hydrophobic compound (3) the effects of the large air-water interfacial adsorption of hydrophobic organics.

Of the known mechanisms for VOC enrichment factors, all may play a role in CWFA system water production. The effects of temperature correction were applied by adjusting the controlling temperature for Henry's Law constant from the chamber air temperature to the coil temperature. The effect of organic matter on the solubility of benzene was considered in this study; however not enough data were collected to show a relationship between organic matter and the enrichment factors observed in the product water. The last mechanism may be of most significance for this study, given the thin film that forms on the evaporator coils of the CWFA system during water production (Figure 13). CWFA systems produce film-wise condensation in which drops initially formed quickly conjoin to produce a semi-continuous film of liquid on the surface pending the availability of water vapor in the air. The thin film layer provides an increase in surface area on which benzene can adsorb. Valsaraj (50) found that the concentration of the dispersed phase of the water-air interface increases as the droplet diameter decreases. This relationship is described in the following equation (50):

$$C_i\ (aq) = C_i^{\ 0}\ (aq) + \left(\frac{6}{dp} \times\ \Gamma_i^{\sigma}\right) \qquad \text{[EQ \#5]}$$

C_i (aq) - molar concentrations (mol m–3) of the species i in the water

$C_i^{\ 0}$ (aq) - concentration (mol m–3) in the bulk water phase (dispersed phase)

Γ_i^{σ}- represents the surface concentration at the air–water interface (mol m–2),

dp - droplet diameter

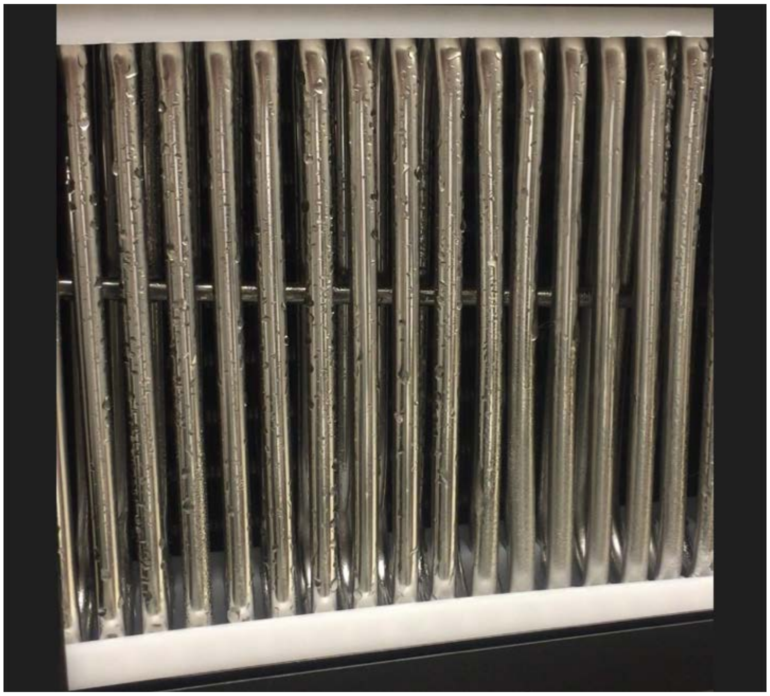

Figure 13. Photo of Thin-Film Condensation on the Evaporator Coils.

Furthermore, it was observed that the CWFA system produced less water at the lower air temperature (25˚C) than higher temperature (35˚C). At 25˚C the CWFA system produced between 200 – 250 mL of water during the one hour sample period. At 35˚C the CWFA system produced between 300 – 400 mL of product water during the one hour sample period. The CWFA system had a one speed controlled fan rate; therefore, a reduced water production at a lower temperature was expected. With a one speed fan, the rate of droplet formation is reduced at a lower temperature, but the mass of benzene passing over the coil is steady. As a result, more benzene mass passed over the thin film interface before the condensation droplet fell into the product water collection container. This mechanism may partially account for the large differences in benzene concentration in the product water observed between 25˚C and 35˚C. Accordingly the additional surface area on condensation droplets and the then film surface as well as the mass transfer of benzene during droplet formation may account for the enrichment factors observed in this study.

Untreated Product Water and Control Water Values

Ideally, control water values would show a stronger agreement between the Henry's Law predictions given air temperature and benzene air concentration. However, in this study, calculated values were 2.5 (50 $\mu g/m^3$) and 3.3 (640 $\mu g/m^3$) times greater than control water values (Figure 14). Predicted values based on Henry's Law calculations were determined given air temperature and benzene air concentration per test conditions. The differences between the calculated and measured control values are most likely the result of inadequate time for benzene to fully diffuse and reach equilibrium through the 300ml volume of the control water in the limited one hour sampling period. As a result, the control water contained less benzene than predicted based on Henry's Law calculations.

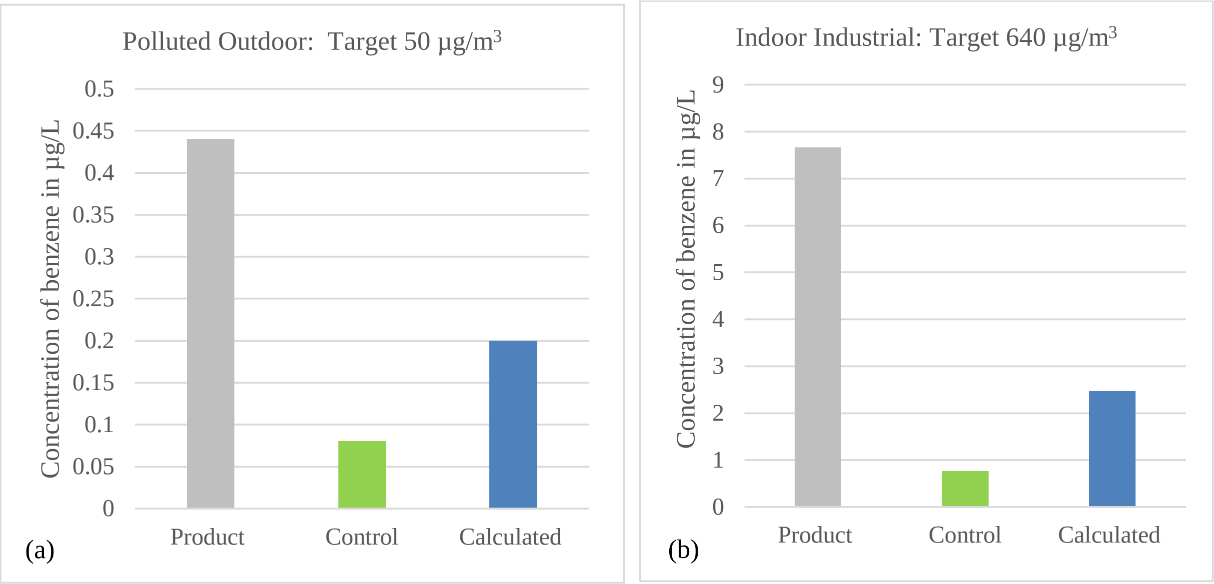

Figure 14. Product vs. Control Water Benzene Concentrations.

The mean benzene concentration for product and control water for full scale conditions (1-4) are displayed. Benzene concentration for product and control water data was normalized using the target air concentration of 50 µg/m^3 (a) and 640 µg/m^3 (b) per test condition. The mean of calculated values are based on chamber air temperature and benzene concentration per test condition.

There was a statistical difference (p = 0.0001) between the means of benzene concentration of the product and control water values. The mean benzene concentration in the product water was 5.5 (50 µg/m^3) and 10.1 (640 µg/m^3) times greater than in the mean control water (Figure 14). One mechanism for increased benzene concentration in the product water is that coil temperature is the controlling temperature at which water vapor condenses. Therefore there are two separate temperature conditions for the control and product water (air and coil temperatures respectively). Considering a lower coil temperature than the higher air temperature, product water that condenses on the coil will hold a larger concentration of benzene than the control water at air temperature, as at higher temperatures benzene will volatilize into the air and less will be contained in the water.

CONCLUSION

Characteristic of what Henry's Law concepts demonstrate, this study found that the temperature and benzene air concentration affected the untreated product water quality from a CWFA system. Accordingly, air temperature affected the concentration of benzene in the product water, with lower temperature having higher product water concentrations. Similarly, increased benzene vapor concentrations resulted in increased concentrations of benzene in the product water. In contrast to the conceptual similarities with Henry's Law, this study found enrichment factors up to 2.1 times greater than what Henry Law calculations predicts.

Benzene vapor concentrations representing a polluted outdoor environment resulted in benzene product water concentrations an order of magnitude below the U.S. military and USEPA drinking water standard of 5 µg/L. (40, 46). In contrast, benzene vapor concentrations representing an indoor industrial environment resulted in benzene product water concentrations up to 100% above the drinking water standard. These findings indicate that both air temperature and air quality should be taken into account during operation of the CWFA system as untreated product water quality will be affected by both air temperature and benzene concentration. This study was limited to testing one contaminant (benzene), which may not represent all VOCs or the impact of interactions between VOC/SVOCs.

There was a substantial difference between the concentrations of benzene in product water compared to control water, with product water having approximately an order of magnitude greater benzene concentration than control water. Though, since the control water was not at equilibrium it is more appropriate to compare Henry's Law calculations to the product water. Product water values always exceeded Henry's Law calculated values based on air and coil temperature [2.9 times (mean overall) and 1.6 times (mean overall)] (Figure 12). This indicates there are additional mechanisms other than temperature and benzene air concentration that impact the concentration of benzene in product water. This study found that Henry's Law equation underestimates the benzene concentration in the product water and may not reflect the actual health risk from drinking this water when operated in a highly polluted environment. A conservative approach to water treatment selection should be applied when CWFA system are operated in indoor industrial settings in order to minimize exposure to benzene from ingestion. Additionally, CWFA system manufacturers should develop special instructions and limitations for highly polluted environments as the maintenance interval of water treatment modules will be shortened in highly polluted outdoor and indoor environments.

CHAPTER 4: CONCLUSION

Condensation Water From Air technology is unique in that the air is a drinking water source. Similar to other drinking water sources, it is necessary to characterize the raw water in order to conduct an appropriate health risk assessment. The goal of this research was to investigate the relationship of benzene vapor concentration and temperature with the concentration of benzene in the untreated product water of CWFA systems. Benzene concentrations representative of a highly polluted outdoor urban environment and indoor industrial environments were used to challenge the CWFA system in an environmental chamber. Air and water samples were collected and analyzed for benzene. The below hypothesis outline the approach used to investigate the relationship between untreated product water of CWFA system, benzene air concentration, and air temperature.

Hypothesis #1: When benzene is present at levels common to current polluted urban outdoor environments it will transfer from the air to the product water at levels that are *below* the maximum concentration level for drinking water standards.

Hypothesis #2: When benzene is present at levels common to current indoor industrial environments it will transfer from the air to the product water at levels that are *above* the maximum concentration level for drinking water standards.

Benzene vapor concentrations representing a polluted outdoor environment resulted in benzene product water concentrations an order of magnitude below the U.S. military and USEPA drinking water standard of 5 µg/L (40, 46). In contrast, benzene vapor concentrations representing an indoor industrial environment resulted in benzene product water concentrations up to 100% above the drinking water standard. These results are characteristic of what Henry's Law concepts demonstrate, high benzene vapor concentrations in air resulted in increased concentrations of benzene in the product water than did lower benzene vapor concentrations.

Hypothesis #3: Changes in temperature influence the accumulation of benzene in product water of the CWFA system.

Air temperature affected the concentration of benzene in the product water, with lower temperature having higher product water concentrations. The lower chamber air temperature (25˚C) had approximately double the product water benzene concentration than the higher chamber air temperature (35˚C) at the same target concentrations (Table 21). This finding is also consistent with what Henry's Law with a temperature adjusted K_H would predict. Higher temperatures increase the potential for benzene vaporization, while lower temperatures retain more benzene in the water. These findings indicate that both air temperature and air quality should be taken into account during operation of the CWFA system as untreated product water quality will be affected by both air temperature and benzene concentration.

Hypothesis #4: There is an increase in the concentration of benzene in the untreated product water compared to the control.

There was a substantial difference between the concentrations of benzene in product water compared to control water, with product water having approximately an order of magnitude greater benzene concentration than control water. Though, since the control water was not at equilibrium it is more appropriate to compare Henry's Law calculations to the product water. Product water values always exceeded Henry's Law calculated values based on air and coil temperature [2.9 times (mean overall) and 1.6 times (mean overall)] (Figure 12). This indicates there are additional factors other than temperature and benzene air concentration that impact the concentration of benzene in product water. This study found that Henry's Law equation underestimates the benzene concentration in the product water and may not reflect the actual health risk from drinking this water when operated in a highly polluted environment. A conservative approach to water treatment selection should be applied when CWFA system are operated in indoor industrial setting in order to minimize exposure to benzene from ingestion. Additionally, CWFA system manufacturers should develop special instructions and limitations for highly polluted environments as the life span of water treatment modules will be shortened in highly polluted outdoor and indoor environments.

ASSUMPTIONS/LIMITATIONS

Benzene air concentration in the environmental chamber was a source of uncertainty in this study. Since air samples were a mixture of grab and hour long samples, there is uncertainty that grab samples were an accurate representation of the total sampling period since they only represent a fraction of the total sample time. Additionally, both the pilot and full scale chamber had high ACH (97 – pilot, 81 – full scale). The grab air sample coefficient of variance for test conditions 1-4 were 25, 68, 37, and 29%, due in part to the automated high ACH rate in the environmental chamber (Table 22). The one hour air sample per test condition provides a more accurate representation of the benzene concentration in the air of the chamber throughout the sample period. The mean of the grab air samples per test condition provide a more accurate representation of the benzene vapor concentration, as compared to the hour long air sample per test condition. The mean of grab air samples for test conditions 1-4 were within: 14.2, 66, 6.3, and 2.4% of the one hour air sample per test condition. Low precision between grab and one hour samples for test condition 2 may have been the result of a change in the calibration zero air gas for one of PIDs prior to the start of discrete sample round 4. In order to perform corresponding analysis, the mean of the grab and one hour air samples have been calculated for each test condition and used to normalize data. The mean benzene vapor concentrations for test conditions 1-4 were 106, 115, 768, and 847µg/m^3. Air data normalization to target benzene air concentrations assumed a linear relationship as prescribed by Henry's Law.

Another study limitation is that only one CWFA system was tested. While CWFA technology use the vapor compression cycle to condense water vapor from the air to create product water, the internal air exchange rate may differ per system along with the coil/condenser design and efficiency. Of final consideration is that this study only routinely tested the air for benzene. Other VOC and SVOCs may have impacted the organic content of the air and solubility of benzene. Coil design and efficiency as well as organic content in the air may have a role in the enrichment factors observed in this study.

FUTURE RESEARCH

Further research is needed to investigate the enrichment factors found in this study. Potential areas of future research include:

1) Additional VOC/SVOC interactions on product water. This study was limited to testing one VOC (benzene). Further investigations are needed to determine if other VOCs and SVOCs have similar enrichment results. The interaction between organics and hydrophobic

compounds should be investigated to determine if solubility of the hydrophobic compound is impacted.

2) Repeatability tests with different CWFA systems. While CWFA systems use the vapor compression cycle to condense water vapor to form liquid droplets, it is important to note that not all condensation systems are the same. Condensation systems vary in design for improvements in energy efficiency including coil and condenser design as well as fan speed modes for low temperature and relative humidity conditions. Follow on investigations testing different CWFA systems would be beneficial to determine if the results of this study can be applied at a broader scale.

3) Untreated product water modeling. This study assumed a linear relationship of benzene vapor concentration to benzene concentration in the product water as prescribed by Henry's Law. However, this study found that temperature adjusted Henry's Law equation underestimates the benzene concentration in the product water. Thus, a follow-on investigation modeling expected untreated product water contaminant concentrations over a larger number of air concentrations would be beneficial to inform health risk assessments prior to operation in a polluted environment.

4) Mechanism determination. Product water values always exceeded Henry's Law calculated values based on coil temperature. Therefore, enrichment factors other than coil temperature and benzene air concentration impact the concentration of benzene in product water. Further investigation is needed at the condensation droplet and thin film interface on the coil to verify the mechanism for enrichment factors responsible for increased concentration of benzene in untreated product water under these conditions.

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APPENDIX A – RAW DATA

Table A-1. Raw Pilot Data

Pilot	**Sample #**	**Concentration of Benzene in the Product Water (µg/L)**	**Concentration of Benzene in the Control Water (µg/L)**	**Benzene Air Concentration (µg/m^3)**
Test 3 25˚C 65% RH Target Benzene Concentration = 50 µg/m^3	Baseline	0.016	0.019	Sample not taken
	1	3.30	0.74	280
	2	3.10	0.75	
	3	2.90	0.85	250
	4	2.80	0.77	
	5	2.80	0.48	280
	6	2.90	0.53	
	Mean	2.97	0.69	270
Test 4 25˚C 65% RH Target Benzene Concentration = 50 µg/m^3	1	2.60	0.79	250
	2	2.80	0.69	
	3	2.40/2.10*	0.43/0.47*	220
	4	2.30	0.34	
	5	2.40	0.50	250/260*
	6	2.40	0.65	
	Mean	2.48	0.57	240

* Duplicate

Table A-2. Full Scale Test Raw Data

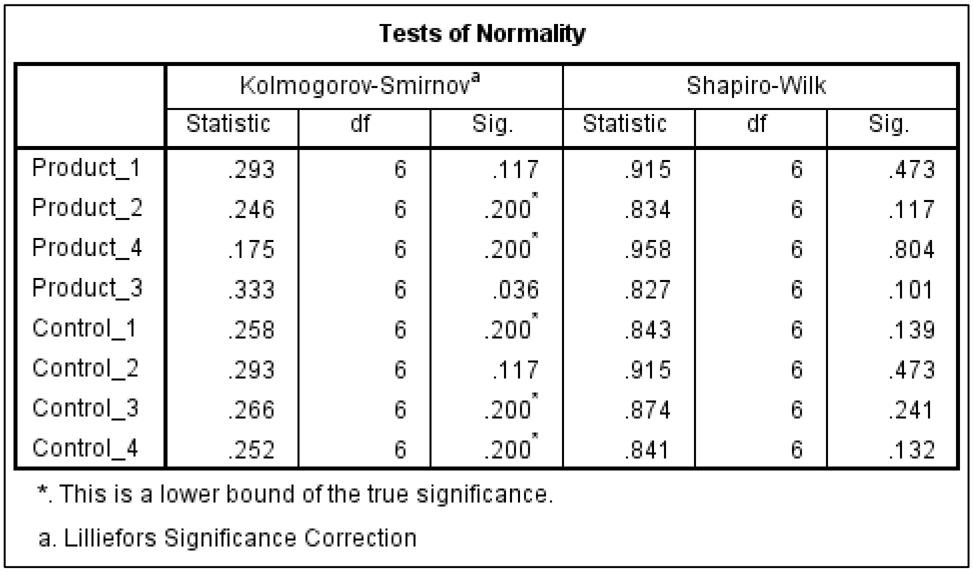
Full Scale Test	**Sample #**	**Concentration of Benzene in the Product Water (µg/L)**	**Concentration of Benzene in the Control Water (µg/L)**	**Benzene Air Concentration (µg/m^3)**
Condition 1 25˚C 45% RH Target Benzene Concentration = 50 µg/m^3	Baseline	0.042	0	3
	1	1.30	0.36	120
	2	1.00	0.15	110
	3	1.20/1.10*	0.17/0.20*	95
	4	1.10	0.17	95/86*
	5	1.10	0.20	120**
	6	1.10	0.26	93
	Mean	1.13	0.22	106
Condition 2 35˚C 45% RH Target Benzene Concentration = 50 µg/m^3	1	0.73	0.09	86
	2	0.87	0.10	110
	3	0.75/0.79*	0.10/0.10*	90
	4	0.78	0.11	170/120*
	5	0.73	0.10	74**
	6	0.71	0.12	160
	Mean	0.76	0.10	115
Condition 3 25˚C 45% RH Target Benzene Concentration = 640 µg/m^3	1	12.0	1.10	820
	2	12.0	1.10	790
	3	13.0/12.0*	0.81/1.00*	760
	4	11.0	1.20	900/900*
	5	12.0	0.78	730**
	6	12.0	0.70	610
	Mean	12.0	0.95	768
Condition 4 35˚C 45% RH Target Benzene Concentration = 640 µg/m^3	1	7.50	1.30	920
	2	6.70	0.86	840
	3	7.20/8.50*	1.60/1.60*	730
	4	6.80	0.66	780/580*
	5	7.20	0.67	830**
	6	7.00	0.60	980
	Mean	7.07	0.95	847

* Duplicate

**One hour sample

APPENDIX B – STATISTICAL ANALYSIS

Table B-1. Normal Distribution Tests



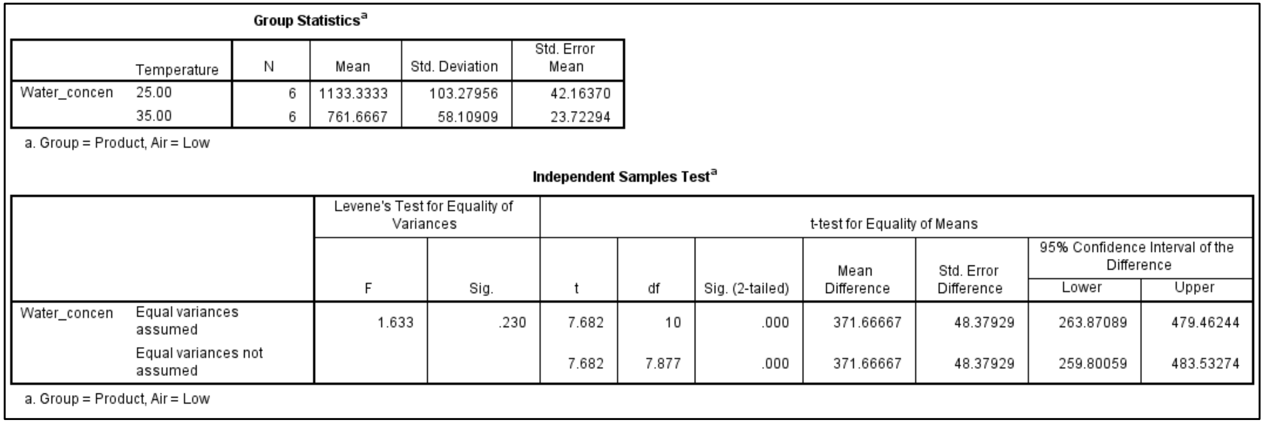
Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Product_1	.293	6	.117	.915	6	.473
Product_2	.246	6	.200*	.834	6	.117
Product_4	.175	6	.200*	.958	6	.804
Product_3	.333	6	.036	.827	6	.101
Control_1	.258	6	.200*	.843	6	.139
Control_2	.293	6	.117	.915	6	.473
Control_3	.266	6	.200*	.874	6	.241
Control_4	.252	6	.200*	.841	6	.132

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

Table B-2. Product Water Temperature T-Tests Analysis – Raw Data (a)



Group Statistics[a]

	Temperature	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	25.00	6	1133.3333	103.27956	42.16370
	35.00	6	761.6667	58.10909	23.72294

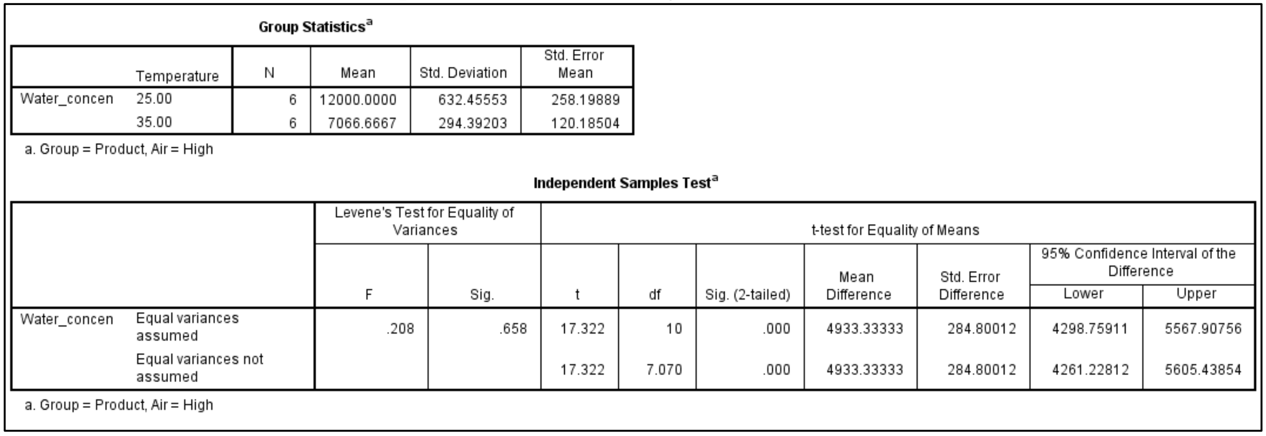
a. Group = Product, Air = Low

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Water_concen	Equal variances assumed	1.633	.230	7.682	10	.000	371.66667	48.37929	263.87089	479.46244
	Equal variances not assumed			7.682	7.877	.000	371.66667	48.37929	259.80059	483.53274

a. Group = Product, Air = Low

Table B-3. Product Water Temperature T-Test Analysis – Raw Data (b)



Group Statistics[a]

	Temperature	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	25.00	6	12000.0000	632.45553	258.19889
	35.00	6	7066.6667	294.39203	120.18504

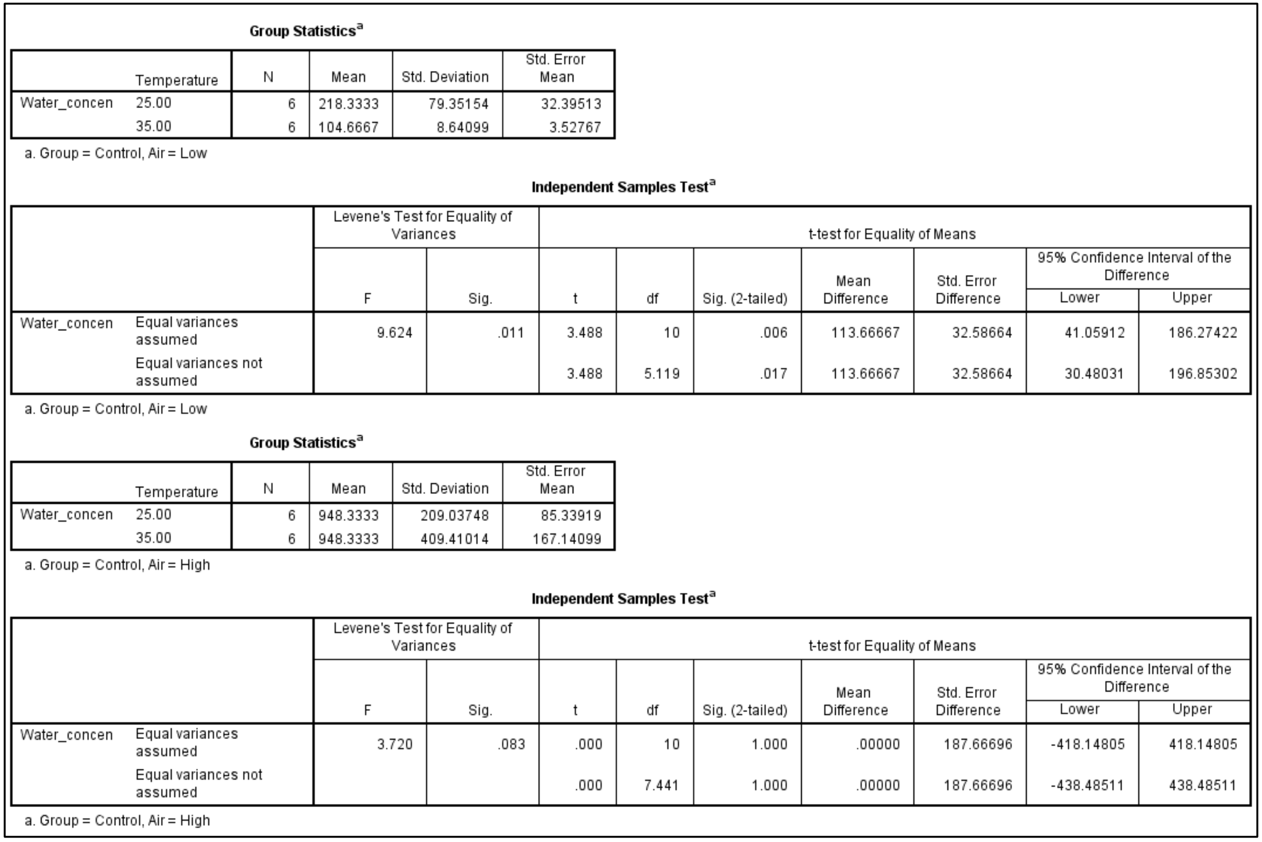
a. Group = Product, Air = High

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Water_concen	Equal variances assumed	.208	.658	17.322	10	.000	4933.33333	284.80012	4298.75911	5567.90756
	Equal variances not assumed			17.322	7.070	.000	4933.33333	284.80012	4261.22812	5605.43854

a. Group = Product, Air = High

Table B-4. Control Water Temperature T-Test Analysis - Raw Data



Group Statistics[a]

	Temperature	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	25.00	6	218.3333	79.35154	32.39513
	35.00	6	104.6667	8.64099	3.52767

a. Group = Control, Air = Low

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Water_concen	Equal variances assumed	9.624	.011	3.488	10	.006	113.66667	32.58664	41.05912	186.27422
	Equal variances not assumed			3.488	5.119	.017	113.66667	32.58664	30.48031	196.85302

a. Group = Control, Air = Low

Group Statistics[a]

	Temperature	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	25.00	6	948.3333	209.03748	85.33919
	35.00	6	948.3333	409.41014	167.14099

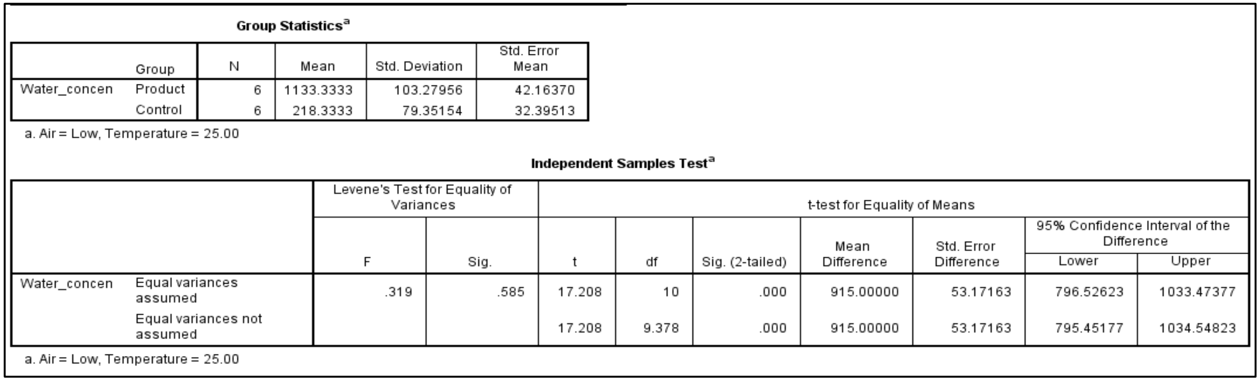
a. Group = Control, Air = High

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Water_concen	Equal variances assumed	3.720	.083	.000	10	1.000	.00000	187.66696	-418.14805	418.14805
	Equal variances not assumed			.000	7.441	1.000	.00000	187.66696	-438.48511	438.48511

a. Group = Control, Air = High

Table B-5. Product vs. Control Water T-Test Analysis – Raw Data (a)



Group Statistics[a]

	Group	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	Product	6	1133.3333	103.27956	42.16370
	Control	6	218.3333	79.35154	32.39513

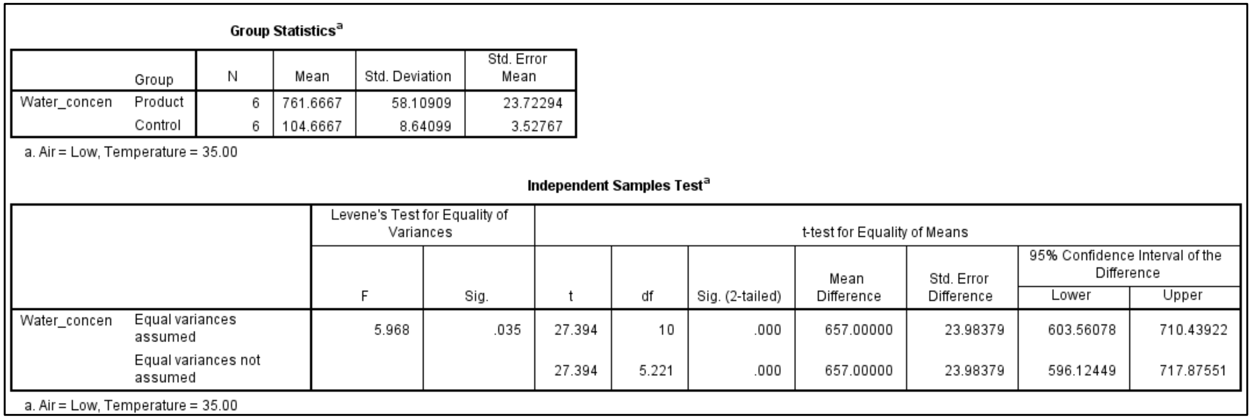
a. Air = Low, Temperature = 25.00

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
									95% Confidence Interval of the Difference	
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	Lower	Upper
Water_concen	Equal variances assumed	.319	.585	17.208	10	.000	915.00000	53.17163	796.52623	1033.47377
	Equal variances not assumed			17.208	9.378	.000	915.00000	53.17163	795.45177	1034.54823

a. Air = Low, Temperature = 25.00

Table B-6. Product vs. Control Water T-Test Analysis – Raw Data (b)



Group Statistics[a]

	Group	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	Product	6	761.6667	58.10909	23.72294
	Control	6	104.6667	8.64099	3.52767

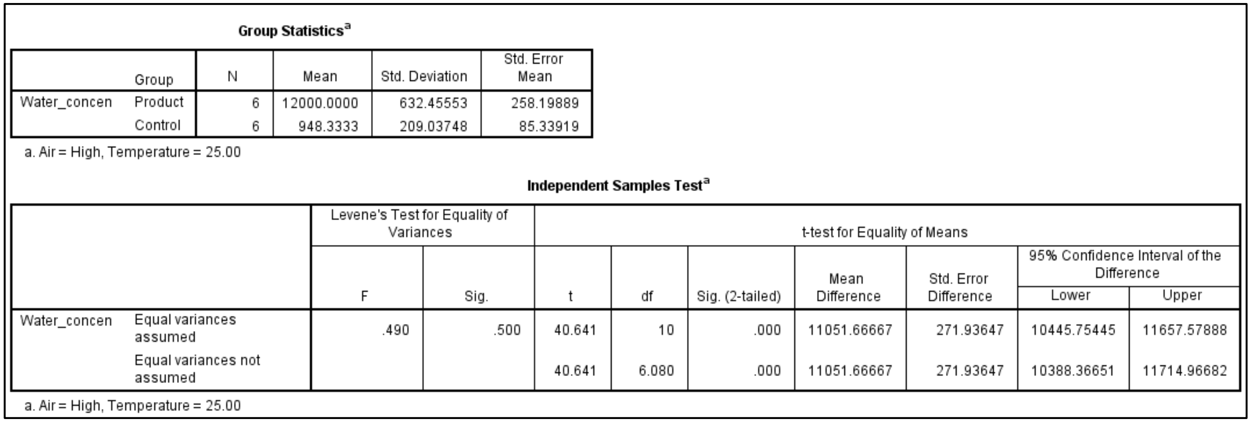
a. Air = Low, Temperature = 35.00

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Water_concen	Equal variances assumed	5.968	.035	27.394	10	.000	657.00000	23.98379	603.56078	710.43922
	Equal variances not assumed			27.394	5.221	.000	657.00000	23.98379	596.12449	717.87551

a. Air = Low, Temperature = 35.00

Table B-7. Product vs. Control Water T-Test Analysis – Raw Data (c)



Group Statistics[a]

	Group	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	Product	6	12000.0000	632.45553	258.19889
	Control	6	948.3333	209.03748	85.33919

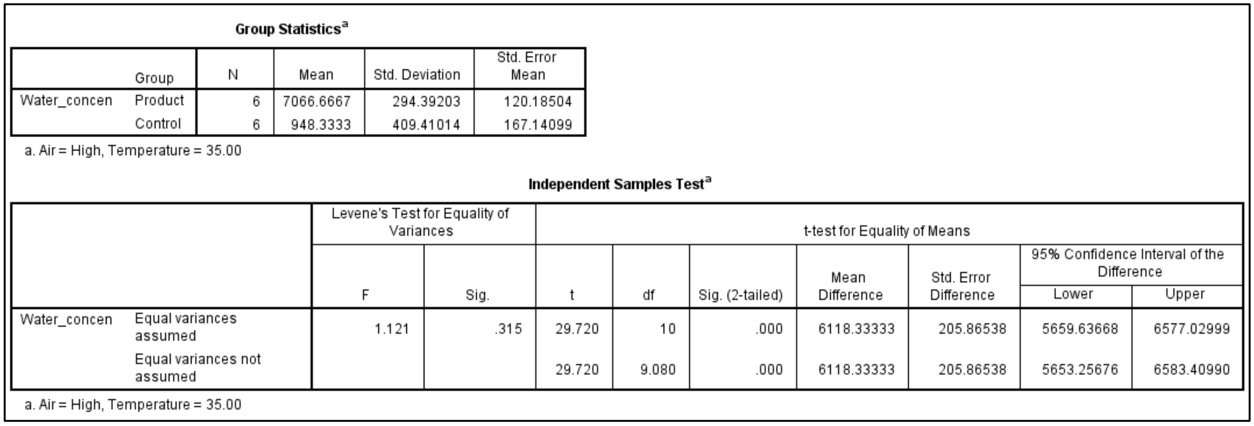
a. Air = High, Temperature = 25.00

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Water_concen	Equal variances assumed	.490	.500	40.641	10	.000	11051.66667	271.93647	10445.75445	11657.57888
	Equal variances not assumed			40.641	6.080	.000	11051.66667	271.93647	10388.36651	11714.96682

a. Air = High, Temperature = 25.00

Table B-8. Product vs. Control Water T-Test Analysis – Raw Data (d)



Group Statistics[a]

	Group	N	Mean	Std. Deviation	Std. Error Mean
Water_concen	Product	6	7066.6667	294.39203	120.18504
	Control	6	948.3333	409.41014	167.14099

a. Air = High, Temperature = 35.00

Independent Samples Test[a]

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Water_concen	Equal variances assumed	1.121	.315	29.720	10	.000	6118.33333	205.86538	5659.63668	6577.02999
	Equal variances not assumed			29.720	9.080	.000	6118.33333	205.86538	5653.25676	6583.40990

a. Air = High, Temperature = 35.00

APPENDIX C – NORMALIZED DATA EQUATIONS

Table C-1. Normalized Data Table.

Test #	Temperature (˚C)	RH (%)	Normalized Benzene Air Concentration (μg/m³)	Mean Concentration of Benzene in the Product Water (μg/L)	Mean Concentration of Benzene in the Control Water (μg/L)
Pilot 3	25	65	50	0.55 ± 0.04	0.13 ± 0.03
Pilot 4				0.52 ± 0.04	0.11 ± 0.03
Condition 1	25	45	50	0.54 ± 0.05	0.10 ± 0.04
Condition 2	35			0.33 ± 0.03	0.05 ± 0.00
Condition 3	25		640	10.0 ± 0.53	0.79 ± 0.18
Condition 4	35			5.34 ± 0.22	0.72 ± 0.31

Pilot 3

Product

$$\frac{3300\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 611.11\frac{ng}{L}$$

$$\frac{3100\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 574.07\ \frac{ng}{L}$$

$$\frac{2900\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 537.04\ \frac{ng}{L}$$

$$\frac{2800\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 518.52\ \frac{ng}{L}$$

$$\frac{2800\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 518.52\ \frac{ng}{L}$$

$$\frac{2900\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 537.04\ \frac{ng}{L}$$

Average = 549.38 $\frac{ng}{L}$ or 0.549 $\frac{ug}{L}$ ± 0.036 $\frac{ug}{L}$

Control

$$\frac{740\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 137.04\ \frac{ng}{L}$$

$$\frac{750\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 138.89\ \frac{ng}{L}$$

$$\frac{850\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 157.41\ \frac{ng}{L}$$

$$\frac{770\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 142.59\ \frac{ng}{L}$$

$$\frac{480\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 88.89\ \frac{ng}{L}$$

$$\frac{530\ ng/L}{270\ ug/m3} \times \frac{50\ ug}{m3} = 98.15\ \frac{ng}{L}$$

Average = 127.16 $\frac{ng}{L}$ or 0.127 $\frac{ug}{L}$ ± 0.027 $\frac{ug}{L}$

Pilot 4

Product

$$\frac{2600\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 541.67\ \frac{ng}{L}$$

$$\frac{2800\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 583.33\ \frac{ng}{L}$$

$$\frac{2400\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 500.00\ \frac{ng}{L}$$

$$\frac{2300\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 479.17\ \frac{ng}{L}$$

$$\frac{2400\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 500.00\ \frac{ng}{L}$$

$$\frac{2400\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 500.00\ \frac{ng}{L}$$

Average = 517.36 $\frac{ng}{L}$ or 0.517 $\frac{ug}{L}$ ± 0.038 $\frac{ug}{L}$

Control

$$\frac{790\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 164.58\ \frac{ng}{L}$$

$$\frac{690\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 143.75\ \frac{ng}{L}$$

$$\frac{430\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 89.58\ \frac{ng}{L}$$

$$\frac{340\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 70.83\ \frac{ng}{L}$$

$$\frac{500\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 104.17\ \frac{ng}{L}$$

$$\frac{650\ ng/L}{240\ ug/m3} \times \frac{50\ ug}{m3} = 135.42\ \frac{ng}{L}$$

Average = 118.06 $\frac{ng}{L}$ or 0.118 $\frac{ug}{L}$ ± 0.036 $\frac{ug}{L}$

Condition 1

Product

$$\frac{1300\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 616.11\ \frac{ng}{L}$$

$$\frac{1000\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 473.93\ \frac{ng}{L}$$

$$\frac{1200\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 568.72\ \frac{ng}{L}$$

$$\frac{1100\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 521.33\ \frac{ng}{L}$$

$$\frac{1100\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 521.33\ \frac{ng}{L}$$

$$\frac{1100\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 521.33\ \frac{ng}{L}$$

Average = 537.125$\frac{ng}{L}$ or 0.54 $\frac{ug}{L}$ ± 0.049 $\frac{ug}{L}$

Control

$$\frac{360\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 170.62\ \frac{ng}{L}$$

$$\frac{150\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 71.1\ \frac{ng}{L}$$

$$\frac{170\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 80.57\ \frac{ng}{L}$$

$$\frac{170\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 80.57\ \frac{ng}{L}$$

$$\frac{200\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 94.79\ \frac{ng}{L}$$

$$\frac{260\ ng/L}{105.5\ ug/m3} \times \frac{50\ ug}{m3} = 123.22\ \frac{ng}{L}$$

Average = 103.48 $\frac{ng}{L}$ or 0.10 $\frac{ug}{L}$ ± 0.038 $\frac{ug}{L}$

Condition 2

Product

$\frac{730\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 317.39\ \frac{ng}{L}$

$\frac{870\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 378.26\ \frac{ng}{L}$

$\frac{750\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 326.09\ \frac{ng}{L}$

$\frac{780\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 339.13\ \frac{ng}{L}$

$\frac{710\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 308.40\ \frac{ng}{L}$

$\frac{730\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 317.39\ \frac{ng}{L}$

Average = 331.16 $\frac{ng}{L}$ or 0.331 $\frac{ug}{L}$ ± 0.026 $\frac{ug}{L}$

Control

$\frac{90\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 39.13\ \frac{ng}{L}$

$\frac{100\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 43.48\ \frac{ng}{L}$

$\frac{100\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 43.48\ \frac{ng}{L}$

$\frac{110\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 47.83\ \frac{ng}{L}$

$\frac{100\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 43.48\ \frac{ng}{L}$

$\frac{120\ ng/L}{115\ ug/m3} \times \frac{50\ ug}{m3} = 52.17\ \frac{ng}{L}$

Average = 44.93 $\frac{ng}{L}$ or 0.05 $\frac{ug}{L}$ ± 0.005 $\frac{ug}{L}$

Condition 3

Product

$\frac{12000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 9{,}996.1\ \frac{ng}{L}$

$\frac{12000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 9{,}996.1\ \frac{ng}{L}$

$\frac{13000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 10{,}829.1\ \frac{ng}{L}$

$\frac{11000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 9{,}163.1\ \frac{ng}{L}$

$\frac{12000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 9{,}996.1\ \frac{ng}{L}$

$\frac{12000\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 9{,}996.1\ \frac{ng}{L}$

Average = 9,996.1 $\frac{ng}{L}$ or 10.0 $\frac{ug}{L}$ ± 0.526 $\frac{ug}{L}$

Control

$\frac{1100\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 916.31\ \frac{ng}{L}$

$\frac{1100\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 916.31\ \frac{ng}{L}$

$\frac{810\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 674.74\ \frac{ng}{L}$

$\frac{1200\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 999.61\ \frac{ng}{L}$

$\frac{780\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 649.75\ \frac{ng}{L}$

$\frac{700\ ng/L}{768.3\ ug/m3} \times \frac{640\ ug}{m3} = 583.11\ \frac{ng}{L}$

Average = 789.94 $\frac{ng}{L}$ or 0.79 $\frac{ug}{L}$ ± 0.174 $\frac{ug}{L}$

Condition 4

Product

$$\frac{7500\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5669.74\ \frac{ng}{L}$$

$$\frac{6700\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5064.97\ \frac{ng}{L}$$

$$\frac{7200\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5442.95\ \frac{ng}{L}$$

$$\frac{6800\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5140.56\ \frac{ng}{L}$$

$$\frac{7200\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5442.95\ \frac{ng}{L}$$

$$\frac{7000\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 5291.76\ \frac{ng}{L}$$

Average = 5342.15 $\frac{ng}{L}$ or 5.34 $\frac{ug}{L}$ ± 0.222 $\frac{ug}{L}$

Control

$$\frac{1300\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 982.75\ \frac{ng}{L}$$

$$\frac{860\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 650.13\ \frac{ng}{L}$$

$$\frac{1600\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 1209.54\ \frac{ng}{L}$$

$$\frac{660\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 498.94\ \frac{ng}{L}$$

$$\frac{670\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 506.5\ \frac{ng}{L}$$

$$\frac{600\ ng/L}{846.6\ ug/m3} \times \frac{640\ ug}{m3} = 453.58\ \frac{ng}{L}$$

Average = 716.91 $\frac{ng}{L}$ or 0.72 $\frac{ug}{L}$ ± 0.31 $\frac{ug}{L}$

APPENDIX D – HENRY’S LAW

Hpc method – for the physical sciences

Example of calculation: Using 25˚C at 120 µg/m^3

HLC (K_H) = $5.56 \times 10^{-3}\ \frac{atm*m3}{mol}$ x $\frac{1000\ L}{1\ m3}$ = $\frac{5.56\ atm*L}{mol}$ or $\frac{1}{\frac{5.56\ atm*L}{Mol}}$ = $\frac{0.1798\ mol}{atm*L}$

$\frac{0.12\frac{mg}{m3}(24.465)}{78.11\ g/mol}$ = 0.0376 PPMV $\times\ (\frac{10-6\ ATM}{1\ PPMV})$ = 3.7585 x 10-9 ATM

Gas $\frac{Mol}{L}$ = K_H (Pg) → $\frac{0.1798\ mol}{L}\ (3.7585\ x\ 10\text{^} - 9\ ATM)$ = $6.757 \times 10^{-9}\ \frac{mol}{L}$

$6.757 \times 10^{-9}\ \frac{mol}{L}\ (\frac{78.11g}{mol})(\frac{1x10\text{^}9\ ng}{g})$ = **527.85** $\boldsymbol{\frac{ng}{L}}$