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Evaluating the impact of ambient benzene vapor concentrations on product water from Condensation Water From Air technology

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HIGHLIGHTS

- Potential for air contaminants to enter drinking water and impact human health
- Environmental chamber tests compared benzene concentrations in air and product water
- Temperature and air quality influence the product water quality of CWFA technology
- Poor air quality may result in product water not meeting drinking water standards.

GRAPHICAL ABSTRACT

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ABSTRACT

Globally, drinking water resources are diminishing in both quantity and quality. This situation has 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 are currently insufficient data available to determine the relationship between air contaminants and the rate at which they are transferred from the air into CWFA untreated product water. This study implemented a novel experimental method utilizing an environmental test chamber to evaluate how air quality and temperature affects CWFA untreated product water quality in order to collect data that will inform the type of water treatment required to protect human health. This study found that temperature and benzene air concentration affected the untreated product water from a CWFA system. Benzene vapor concentrations representing a polluted outdoor environment resulted in benzene product water concentrations between 15% and 23% of the USEPA drinking water limit of 5 µg/l. In contrast, product water benzene concentrations representing an indoor industrial environment were between 1.4 and 2.4 times higher than the drinking water limit. Lower condenser coil temperatures were correlated with an increased concentration of benzene in the product water. Environmental health professionals and engineers can integrate the results of this assessment to predict benzene concentrations in the product water and take appropriate health protective measures.

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1. Introduction

Globally, 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. Currently, this technology generates water from atmospheric moisture in military, commercial, industrial, and residential applications. For example, the United States Army is interested in developing WFA technology to improve logistical efficiencies that reduce reliance on intermediate staging bases and sustainment logistics in remote, austere environments. The ideal WFA technology would improve the Army's ability to conduct military operations by bringing water production and purification closer to the point of need and thereby improve unit self-sufficiency (Army Capabilities Integration Center, 2014). Past studies have investigated the efficiency of CWFA systems (Peters et al., 2013; Walhgren, 2001). Current CWFA systems have a high-energy requirement that make the technology attractive only in situations in which water is expensive to procure or not readily available due to source or infrastructure limitations. However, given growing global concerns about water scarcity and drinking water shortages, interest in this technology has grown and improvements to energy efficiency for WFA technology is being sought by industry. Between 2015 and 2022, the global WFA market is expected to grow 37.4%, with drinking water programs in Japan and India investigating policies for this use of this technology (GlobeNewsWire, 2016). In the United States, the Monterey Peninsula Water Management District Board of Directors recently approved the use of WFA technology as the sole water source option for businesses or secondary buildings (Whittaker, 2014). WFA technology is receiving greater interest and its increased efficiency is making it a more practicable option for water production. Therefore, it is important to determine how airborne contaminants impact the product water quality of WFA technology in order to select the most appropriate water treatment technologies that maximize technology efficiencies while protecting health.

Potential applications of WFA technology include worldwide use in outdoor and indoor environments. Of the outdoor environments, megacities may be the most significant. Megacities are dense urban environments comprised of populations > 10 million. By 2030 60% of the world's population is projected to live in urban environments that may be congested and highly polluted (Department of the Army, 2014). 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 (Chittaranjan-Tembhekar, 2013). WFA technology applications in indoor settings are also important because industrial processes such as automotive repair and painting operations can create air quality that has the potential to be extremely poor. Currently, there are limited regulatory or manufacturer specific guidelines or special considerations for the prolonged operation and maintenance of the WFA water treatment systems in either indoor or outdoor settings. Thus, it is important to characterize the quality of drinking water produced from WFA technology when used in highly polluted environments.

The WFA systems extract water from the air for both potable and non-potable purposes. The WFA technology concept is not new, with feasibility experiments dating back >45 years (Hellström, 1969). The two most common types of these systems utilize either condensation or desiccant technology. Condensation Water From Air (CWFA) systems operate by condensing water vapor on an evaporator coil 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 and depends on the amount of humidity in the atmosphere. The compressor, condenser, evaporator, and a liquid medium in the CWFA systems are the primary components essential to the vapor compression cycle and process

airflow 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 condensation systems are the same. Condensation systems vary in design for improvements in energy efficiency, coil design, fan speed, 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 is not required to meet the EPA drinking water standards (USEPA, 2009). As a drinking water source, there is a necessity to determine how product water quality from CWFA systems compares to EPA drinking water standards to characterize health risk. However, there are currently insufficient data available to determine the rate of transfer between air contaminants and CWFA product water. Also absent is a method to predict the transfer of air contaminants into the product water under specified environmental conditions (air temperature, humidity and contaminant concentrations). Although most WFA systems incorporate treatment modules to remove water contaminants, there is uncertainty regarding the appropriate level and maintenance interval of water treatment modules required to minimize the health risk of ingesting product water from CWFA systems given such a wide array of potential environments with different and fluctuating air quality compositions. Walhgren's (2001) review on WFA technology indicated that water produced from the atmosphere may not be safe to drink without treatment. Gandhidasan and Abualhamayel (2010) specified that in polluted urban and industrial environments, water quality of desiccant WFA systems may be compromised and should be monitored. Although neither the aforementioned articles indicated the type of contaminants that may be a health concern, volatile organic compounds (VOC), such as benzene, are common contaminants in those environments.

Benzene (C_6H_6) 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 (ATSDR, 2007). According to the ATSDR (2007), the most significant health effect of benzene is that it is a carcinogen with chronic exposures having the greatest effect on the immune and hematopoietic system due to benzene metabolite effects on the bone marrow. While no human studies have investigated the potential for carcinogenicity due to benzene ingestion, several animal studies have found evidence of benzene acting as a multiple site carcinogen (Huff et al., 1989; Maltoni et al., 1983). Benzene's physical characteristics, likelihood of presence in both indoor industrial and outdoor urban environments, and potential adverse health effects made it the optimal VOC contaminant of concern for this study.

Previous studies have tested the water quality of WFA systems (Bautista-Olivas et al., 2014; Gandhidasan and Abualhamayel, 2010; U.S. Army Institute of Public Health (USAIPH), 2011; Walhgren, 2001). However, no studies have quantified the relationship of temperature with air quality data and its impact on WFA product water quality. Thus, airborne benzene in polluted environments may be a significant concern since it is expected to transfer from the air to the product water of CWFA systems. Accordingly, there is a need for research to determine the best method to predict the transfer of VOCs in the air to CWFA system product water. Henry's Law provides a simple, but potentially useful, method to predict the concentration of water contaminants using only the partial pressure of the gas and the Henry's Law constant (K_H), which is contaminant and temperature dependent (Supplementary materials). Air temperature is the easiest to measure in field settings; however, CWFA coil temperature may be a better predictor of benzene concentrations in product water. Saturation temperature can be used as a predictor for CWFA system coil temperature by means of both relative humidity (RH) and air temperature.

A literature search of global ambient benzene concentrations in outdoor urban as well as indoor industrial environments resulted in the selection of appropriate benzene vapor concentrations to be used in experimental testing. The literature indicated that outdoor urban and indoor industrial concentrations of benzene vary significantly across

the globe. Table 1 provides a summary of these air concentrations. Developing nations with new or absent air quality regulations and occupational safety standards had the greatest concentrations of benzene in the ambient air and in indoor industrial environments. Given the wide range of benzene concentrations found in the literature, $50 \mu\text{g}/\text{m}^3$ was chosen to represent a polluted outdoor environment. That concentration is above the mean and median outdoor values in Table 1 but was within the range found in literature and above the detection limit for instrumentation used in this study. A benzene vapor concentration of $640 \mu\text{g}/\text{m}^3$ was chosen to represent an indoor industrial environment since it was between the mean and the median of the values found in literature.

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 air temperature with the concentration of benzene in untreated product water, (2) determine whether Henry's Law is a suitable tool to predict benzene concentration in product water using both the air and coil temperatures.

2. Materials and methods

2.1. Experimental set-up

An environmental chamber maintained benzene vapor concentrations, temperature, and RH at steady state conditions. Fig. 1 shows a schematic diagram of the environmental chamber set-up. The environmental chamber measured $2.56 \text{ m} \times 1.07 \text{ m} \times 1.20 \text{ m}$ or a total volume of 3.13 m^3 , adjusted for equipment inside 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). Unfiltered indoor air entered the chamber at a flow rate of 81 air changes per hour (ACH). Due to the nature of the chamber design, the air flow 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 passed through a carbon filter to remove organic impurities prior to entering the chamber. Baseline product and control water analyses at the start of the pilot and full-scale tests (Supplementary materials, Tables SM.1, SM.2) indicate that the tap water used to generate humidity had minor influence on the control and product water results during testing. Temperature in the chamber was also automated and controlled by refrigeration and nichrome heating elements.

Benzene was introduced into the chamber using a certified compressed gas cylinder of 1.01 mol% concentration at a pressure of 1.266 kg per square centimeter and a rate controlled by a calibrated, mass flow controller. 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.

The system selected to generate untreated product water for this study was the AquaBoy™, a small scale (up to 20 l per day), commercially available CWFA system. Atmospheric Water Solution, Inc. designed the AquaBoy™ for use in residential and office buildings. To evaluate the untreated product water, the CWFA system water treatment module was removed from the system. A calibrated thermocouple temperature logger, secured to one point on the center of the outer evaporator coil in the CWFA system, monitored coil temperature. A calibrated hand held humidity and temperature meter 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.

2.2. Experimental procedure

2.2.1. The pilot phase

This study implemented a novel experimental method to test the product water of a CWFA system at known benzene air concentrations in an environmental chamber. The primary purpose of the pilot test was to determine equipment limitations, variation in the experimental method, and calculate an appropriate sample size for the full-scale test. 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 RH and temperature conditions (Table 2). Pilot test 1 determined the lowest chamber air temperature and RH at which the system could produce water was 25°C at 45% RH, with temperature as the limiting condition. Below this air temperature the product water froze on the evaporator coils, which prevented water production. The highest temperature and RH at which the AquaBoy™ system could operate was determined to be 35°C at 65% RH with a control panel high temperature error warning above this set point. The difference in operating temperature range between the manufacturer specifications (15°C – 35°C) and this experiment (25°C – 35°C) may be due to the system modifications for this study. The AquaBoy™ was intended for indoor residential and light commercial use with the water treatment module installed. Each CWFA system temperature operating range is manufacturer and intended purpose specific.

The environmental test chamber was limited to achieving RH parameters between 40 and 80%, with the most stable RH zone between 45 and 50% ($\pm 5\%$). Pilot test 2 determined the rate of benzene required to maintain a steady state of benzene in the chamber given the chamber air exchanges per hour and the CWFA system removal of both water and benzene from the air. Pilot test 3 product water data was analyzed to calculate an appropriate power and sample size utilizing the statistical analysis software (SAS) program version 9.3 for Windows. Pilot test 3 experimental data revealed environmental chamber limitations resulting in increased RH variation at 65% ($\pm 7\%$) over the target RH variation of ($\pm 5\%$).

2.2.2. The full-scale phase

The pilot phase informed the full-scale phase with a few improved procedures and expanded experimental conditions. The full-scale phase consisted of 24 discrete one-hour sampling rounds that split into four separate test conditions, each consisting of six discrete one-hour sample rounds. Testing for each condition took place over a period of 2–3 days. Figs. 1 and 2 show the set-up of the full-scale phase tests in the environmental chamber. Based on pilot study experiments and equipment limitations it was determined that the full-scale testing would use two air temperature conditions, a low (25°C) and high (35°C) value; a constant relative humidity (45%); and two benzene vapor concentrations representing polluted outdoor ($50 \mu\text{g}/\text{m}^3$) and an indoor industrial ($640 \mu\text{g}/\text{m}^3$) environments. Benzene concentrations were monitored using two photoionization detectors (PID) with

Table 1
Summary of ambient outdoor and indoor benzene vapor concentrations.

Environment	High ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Low ($\mu\text{g}/\text{m}^3$)
Polluted outdoor Khoder (2007), Liu et al. (2000), Na et al. (2001), Ohura et al. (2006), Srivastava et al. (2006), Wang and Zhao (2008)	87.2	25.2	20.6	0.48
Indoor industrial de Oliveira et al. (2007), Sheehan et al. (2010), Soldatos et al. (n.d.), Vitali et al. (2006)	7040	1463	540	108

Fig. 1. Schematic diagram of the environmental chamber set-up for the study. 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, 15. air intake, 16. outer building, 17. air exhaust (with filter and blower).

parts per billion (PPB) probes 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 benzene correction factor (0.5) 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 s during every one-hour discrete sampling round. Both PID air monitors were calibrated at the start of every new test condition except for test condition 2. The high calibration point was certified gas standard 7.5 ppm and low calibration point was zero air, certified gas standard. One PID was placed next to the air intake of the CWFA system while a second PID was placed on the opposite side of the environmental chamber to evaluate distribution of benzene in the chamber.

Prior to the start of testing each day, the chamber was operated at 49 °C for 15 min to volatilize and exhaust excess benzene from the chamber and CWFA system. The control beaker containing 300 ml of deionized water was placed into a 1 l beaker to mimic conditions of the product water beaker, which was placed below the evaporator coils inside of the CWFA system. Both beakers were left open to the atmosphere to closely imitate the practical conditions in which CWFA systems are operated. Upon experiment set-up, the chamber and system were stabilized for at least 20 min 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 one-hour sample and replaced below the evaporator for the next sample. The control water beaker

was completely emptied and refilled with deionized water after each one-hour sample.

2.3. Data collection and analytical methods

2.3.1. Air data collection

In addition to direct benzene air monitoring with the PIDs, collection of indirect benzene samples during each discrete sampling round utilized 6.0 liter (l) pre-cleaned and pre-evacuated summa canisters. Each summa canister was connected to 50.8 mm of 6.35 mm inner diameter (ID) × 9.53 mm OD Tygon tubing that connected to 0.6 m of 3.18 mm OD Teflon tubing that was routed through the sampling port hole into the environmental chamber. The summa canister air sample was collected within 6 in. of the air intake of the CWFA system. During testing, five of the six discrete air samples collected per condition (one per sampling round) consisted of 30 s grab samples with the remaining discrete air sample collected over the one-hour sampling period (Table 3). The critical orifice was removed from the summa canister to facilitate a 30 s grab sample of 6.0 l. The one-hour sample was collected at a flow rate of 70 ml (ml)/min. The purpose of the hour-long sample per test condition was to verify the reliability of the 30 s grab samples. Summa canisters were analyzed by using U.S. EPA method TO-15 with gas-chromatography–mass spectrometry (GC–MS) (USEPA, 1999). The mean coefficient of variance between duplicate summa canister grab samples was $16 \pm 14\%$.

2.3.2. Water data collection

The 400-ml control and product water glass collection beakers were washed in laboratory detergent and rinsed with tap water at the start of every test day. Additionally, both beakers were baked at a temperature of 121 °C for 15 min before placing them into the environmental chamber. At the end of the one-hour sample period, water samples were collected utilizing the chamber hand inserts to transfer water into 40 ml glass vials with Teflon® septa. Water samples were analyzed for benzene every sample round (24 samples) (Table 3). The 40 ml sample glass vials were prepared with a 1:1 hydrochloric acid solution to lower the pH ≤ 2 and preserve the sample. The 40 ml glass vials were filled in a manner to minimize agitation and filled to avoid any headspace. After sampling was complete, the 40 ml vials were placed into a portable cooler kept between 0 and 4 °C for transport to the laboratory for analysis. Analytical procedures for the determination of benzene utilized the U.S. EPA Method 524.2 in selected ion monitoring mode (SIM) with gas-chromatography–mass spectrometry (GC–MS) (USEPA,

Table 2
Summary of pilot tests.

Pilot Test	Type of test	Chamber benzene concentration (µg/m ³)	Chamber air temperature (°C)	Relative humidity (%)	Discrete 1 h sampling rounds
1	T and RH verification	None	15.5–35	45–90	NA
2	Steady state	50	25, 35	45, 65	NA
3	Sample size determination	50	25	65	12

Fig. 2. Environmental chamber set-up with the water from air system (left), control water (center) and benzene sampling vials (right).

2005). The mean coefficient of variance between duplicate water samples was $6.7 \pm 5.5\%$.

2.4. Data processing and analysis

The Shapiro-Wilk Test was run to determine if the data followed a normal distribution. A *t*-test was used for three analyses: to determine if there was a statistical difference between the means of the product and control water samples at identical benzene vapor concentrations, to detect a difference between the means of product water benzene concentrations at two different temperatures, and to detect a difference between the means of benzene concentration in the product water at two different target benzene vapor concentrations.

3. Results and discussion

3.1. Influence of benzene vapor concentration and temperature on product water

Analysis of the benzene vapor concentrations variance occurred after the experimental runs were completed. The high amount of variance in the data for the 30-second grab air samples were due in part to the automated high airflow rates in the environmental chamber making them unreliable as a representative snapshot of the entire sampling period. The summa canister duplicate grab air samples taken consecutively versus simultaneously confirm air variations over short periods of time (30 s–1 min). However, the steady state of the PID readings and benzene mass flow rate throughout test indicate that the fluctuation in benzene air concentrations were transitory (Table 4). The one-hour summa canister air sample per test condition provides a more accurate representation of the benzene vapor concentration of the chamber throughout the sample period as compared to the 30 s grab samples

(Supplementary materials, Table SM.3). The mean of the grab air samples per test condition provides a more comprehensive representation of the chamber benzene vapor concentration over the entire test period, using the hour-long air sample as an indicator for the consistency of the mean grab air samples. Table 4 provides a test condition summary of variability in Summa canister air samples, PID readings, the average range of benzene mass, RH, and temperature.

During steady state air temperature and RH conditions, the benzene concentration in CWFA system untreated product water was dependent on the concentration of benzene in the air (Table 5). *t*-Test statistical analysis demonstrated a statistically significant difference ($p = 0.0001$) between the mean concentrations of benzene in product water created at benzene vapor concentrations of outdoor polluted and indoor industrial environments. 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.

The PID readings (Table 4) were consistent and a good indicator for benzene steady state concentration in the chamber, but did not accurately reflect when target benzene concentrations had been reached. In the environmental chamber the mean benzene vapor concentrations representing both the polluted outdoor and indoor environments at 25 °C and 35 °C (Table 5) exceeded the target benzene vapor concentrations of 50 $\mu\text{g}/\text{m}^3$ and 640 $\mu\text{g}/\text{m}^3$, respectively. Although above the targeted concentrations, the chamber mean benzene vapor concentrations are useful since they still allow for a comparison between vapor and product water benzene concentrations. When comparing the chamber benzene concentrations to the literature (Table 1) the outdoor environment values are above the maximum value but the indoor environment values are between the mean and median values found in the literature.

Even with a higher benzene vapor concentration representing a polluted outdoor environment, product water benzene concentrations were 23% (25 °C) and 15% (35 °C) of the USEPA water limit of 5 $\mu\text{g}/\text{l}$ (USEPA, 2009) (Fig. 3). Product water benzene concentrations representing an indoor industrial environment were 2.4 (25 °C) and 1.4 (35 °C) times the drinking water limit, respectively (Fig. 3). There was a statistically significant difference ($p = 0.0001$) between the mean benzene concentration of product water and chamber air temperatures of 25 °C and 35 °C for both polluted outdoor and indoor industrial environments. This analysis is conservative since benzene vapor concentrations were higher during the 35 °C test conditions (Table 5). Nevertheless, the lower chamber air temperature (25 °C) had approximately 1.5 times the product water benzene concentration than the higher chamber air temperature (35 °C) for both polluted outdoor and indoor industrial environments. Conceptually, this finding is consistent with what Henry's Law would predict in that higher temperatures increase the potential for benzene vaporization, while at lower temperatures more benzene is retained in the water.

3.2. Untreated product water vs calculated Henry's Law values

This study utilized Henry's Law as a benchmark to estimate benzene concentration in the product water based on benzene vapor concentration as well as both the coil and air temperatures. Henry's Law is a simple method to estimate benzene concentration in water since all that is required is temperature and benzene vapor concentration. Since water vapor from the air condenses on the evaporator coils of the CWFA system at or below the saturation temperature, coil temperature may be the controlling temperature for the Henry's Law constant used in this study. Fig. 4 compares benzene product water concentrations to the Henry's Law calculated values. When chamber air temperature along with benzene vapor concentration were incorporated into the Henry's Law equation, measured product water values were 2.2 to 3.6 times greater than calculated product water values for conditions 1–4 (Supplementary materials, Table SM.4). Measured product water values also exceeded Henry's Law calculated product water values using coil

Table 3
Number and type of samples collected for the full-scale tests.

Test conditions 1–4	Base-line	Method 524.2 SIM water samples (benzene)	Method TO-15 grab air samples	Method TO-15 1 h air samples
Samples taken				
Control water	1	24 4 duplicates 4 blanks	–	–
Product water	1	24 4 duplicates 4 blanks	–	–
Summa canister	1	–	20 4 duplicate	4

Table 4

Summary chart of data variability during test conditions 1–4.

	^a Summa canister method TO-15 ($\mu\text{g}/\text{m}^3$)	PID ($\mu\text{g}/\text{m}^3$)	^b Benzene mass range (ml/min)	RH (%)	Air temperature (°C)	Coil temperature (°C)
Test condition 1						
Mean	106	50.6	5.10–5.42	45.3	25	10.8
CI 95%	96.1–115	50.2–50.9	NA	44.9–45.6	25.0–25.0	10.4–11.2
Test condition 2						
Mean	115	52.8	5.13–5.90	44.2	35.1	22.3
CI 95%	85.4–145	52.5–53.4	NA	44.0–44.4	35.1–35.1	22.1–22.5
Test condition 3						
Mean	768	638	39.8–37.5	45.7	25.1	12.9
CI 95%	697–839	636–640	NA	45.3–46.1	25.1–25.2	12.6–13.2
Test condition 4						
Mean	847	661	40.2–41.9	44.6	35	22.8
CI 95%	780–913	660–661	NA	44.3–44.9	35.0–35.0	22.7–23.0

^a Mean includes the 1 hour sample and the 30-second grab air samples.^b Values provided are the mean range of benzene mass per test condition.

temperature (ranging from 1.3 to 2.0 times greater) measured in each test condition (Supplementary materials, Table SM.4). While all measured product water values were greater than calculated values using both coil and air temperature, coil temperature more accurately predicted product water concentrations.

Since all measured benzene product water concentrations were greater than Henry's Law calculated values, once explanation is that the actual coil temperature may have been lower than the data measured from a single point on the coil (Supplementary materials, Tables SM.7–10). This may indicate that the temperature was not equally distributed across the coil. For the outdoor air vapor concentrations, mean product water concentrations would have matched calculated values at slightly lower coil temperatures of 7 °C and 17 °C for test conditions 1 and 2, respectively (Table 6). During a different, unpublished study using the same CWFA system, a coil temperature of 7 °C was observed while operating under the same temperature and RH as test condition 1 (Elyamani, 2017). The difference in calculated coil temperature required to match the product water values is greater for indoor industrial vapor concentrations. A mean coil temperature of approximately –2 °C and 11 °C for test conditions 3 and 4, respectively, would have been required to produce measured product water values (Table 6). These lower coil temperatures are not as likely, indicating that product water at indoor industrial benzene vapor concentrations may not have been at equilibrium and was potentially supersaturated with benzene. For this reason, Henry's Law calculations using both air and measured coil temperatures were not an accurate tool to predict the initial concentration of benzene in product water and a supersaturation factor should be considered.

The system produced less water at the lower air temperature (25 °C) than higher temperature (35 °C) because at a steady RH, the atmosphere at 35 °C has a higher absolute humidity and the ability to hold more moisture. This study observed 200–250 ml of water production during the one-hour sample period at 25 °C and 300–400 ml at 35 °C (Supplementary materials, SM.3). Given the steady rate of air flow

through the CWFA system (109m³/h) during all test conditions, the rate of water droplet formation is reduced at lower temperatures, but the mass of benzene passing over the coil and condensing is constant at steady state conditions.

Direct condensation is a potential supersaturation factor that may be significant when determining VOC product water concentrations in CWFA systems. Direct condensation is a VOC recovery technique used by many chemical processing industries to meet air quality standards (Dwivedi et al., 2004; Gupta and Verma, 2002; Khan and Kr. Ghoshal, 2000). The VOC direct condensation process used in industry is similar to the operation of the CWFA system in that air is passed through a heat exchanger (condenser) that cools a vapor below the VOC boiling point, condensation occurs, and the condensate is collected for reuse or disposal (Khan and Kr. Ghoshal, 2000). Water may also condense and be collected along with the VOC during this process but it is usually an undesirable byproduct due to additional treatment costs.

Previous studies that modeled different VOC capture processes indicate that direct condensation on an industrial scale is most efficiently applied with cryogenic temperatures and high vapor concentrations > 5000 ppm (Dwivedi et al., 2004; Khan and Kr. Ghoshal, 2000). Since the CWFA coil temperatures are substantially below benzene's boiling point of 80.1 °C, it is possible that a very small percentage of the benzene mass in the air could directly condense onto the coil and into the product water. The potential for a small portion of the benzene mass to transfer to the CWFA product water in this manner was calculated via the volume ratios between processed air and amount of condensed water. Table 7 summarizes the calculations (Supplementary materials, Eqs. (2)–(4)) to determine the percentage of the total benzene mass passing through the CWFA system that concentrated in the product water.

Given the theoretical mass of benzene that passed over the condenser, the potential for oversaturated product water is likely even if only a very small fraction of the benzene vapor directly condenses into the product water. Since the CWFA coil temperatures are substantially

Table 5

Temperature and benzene vapor concentration affect on product water from CWFA system and the control. Results represent mean and confidence interval (CI 95%) values, RH constant at 45%.

Test Condition	Temperature (°C)	^a Benzene vapor concentration ($\mu\text{g}/\text{m}^3$)	Benzene in the product water ($\mu\text{g}/\text{l}$)	Benzene in the product water CI (95%) ($\mu\text{g}/\text{l}$)	Benzene in the control water ($\mu\text{g}/\text{l}$)	Benzene in the control water CI (95%) ($\mu\text{g}/\text{l}$)
1	25	106	1.13	1.06–1.2	0.22	0.16–0.28
2	35	115	0.76	0.72–0.80	0.10	0.09–0.11
3	25	768	12.0	11.5–12.5	0.95	0.80–1.10
4	35	847	7.07	6.85–7.29	0.95	0.65–1.25

^a Mean values from Table 4.

Fig. 3. Bar graphs of the benzene concentration in product water at 25 °C and 35 °C given average benzene vapor concentrations in a polluted outdoor environment (a) an indoor industrial environment (b). Standard deviations of the product water data are shown.

below benzene's boiling point of 80.1 °C, it is possible that a very small percentage of the benzene mass in the air could directly condense onto the coil and into the product water. Consistent with industrial direct condensation VOC capture processes, this study observed that a larger fraction of benzene condensed at high benzene vapor concentrations compared to the low benzene vapor concentrations (Dwivedi et al., 2004; Khan and Kr. Ghoshal, 2000). Additionally, at the high benzene vapor concentrations, a larger fraction of benzene condensed at the lower coil temperature but this temperature relationship was not observed at low benzene vapor concentrations (Table 5).

CWFA systems produce film-wise condensation on the evaporator coil. Drops initially formed quickly and conjoined to produce a semi-continuous film of liquid on the surface of the coil. The rate of droplet formation depends on the amount of water vapor in the air. This thin film layer provides a large surface area relative to water volume on which benzene can adsorb and quickly reach equilibrium. If a small amount of benzene directly condenses on the coil it may increase the thin film benzene concentration above saturation. If the thin film of water on the coil quickly forms drops and enters the product water container, the supersaturated water accumulates and time for product water concentrations to decrease to equilibrium state is influenced by the ratio of surface area to total product water volume and the low water temperature (approximately coil temperature) relative to air temperature. Although the volume ratios of air to condensed product water indicate that only a small fraction of benzene vapor may have condensed into the product water, lower condensing temperatures and/or higher concentrations of benzene vapor increased the fraction

of benzene that directly condenses into the water and increase the health risk of untreated product water.

3.3. 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 per test condition. However, in this study, calculated control water values for a polluted outdoor environment were 2.1 (25 °C) and 3.4 (35 °C) times greater than actual control water values. Similarly, calculated control water values for an indoor industrial environment were 3.6 (25 °C) and 2.9 (35 °C) times greater than actual control water values (Fig. 5). 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 300 ml volume of the control water in the limited one-hour sampling period. Unlike the thin film on the coil during product water formation, the control water samples have a much lower ratio of surface area to volume. Therefore, the time required to reach equilibrium is expected to be much greater than 1 h for the control water samples. Thus, the control water contained less benzene than predicted based on Henry's Law calculations. Additionally, there was a statistically significant difference ($p = 0.0001$) between the mean benzene concentration of the product water and calculated control water values. The mean product water benzene concentration in a polluted outdoor environment was 2.4 (25 °C) and 2.2 (35 °C) times greater than the mean of calculated control water values (Fig. 5). Similarly, mean product water benzene concentration in an indoor industrial environment was 3.6 (25 °C) and 2.5 (35 °C) times greater than the mean of the calculated control water values.

The difference in benzene concentrations between the product water and control water samples is likely related to temperature differences in the samples. The product water is generated at the lower coil temperature while the control water in the beaker is at the higher air temperature. The product water that condenses at the lower coil temperature is able to hold a larger concentration of benzene than the control water, which is at the higher air temperature. As water temperature

Fig. 4. Measured product water values, coil temperature and air data from the one-hour air sampling period (sample 5) 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.

Table 6

Calculated coil temperatures required to reach measured benzene concentrations in the product water.

Test condition	Measured coil temp (°C)	Calculated coil temp (°C)	Difference
1	11	7	4
2	22	17	5
3	13	−2	15
4	23	11	12

Table 7

Summary of the percent of benzene in the product water for test conditions 1–4. The percentage of benzene mass (P_b) in the air that transfers to the product water during each sampling period was calculated given eq. 2–4 (Supplementary materials).

Test condition	Air temp (°C)	Coil temp (°C)	^a C_a (μg/m ³)	^b M_a (μg)	^c V_w (l)	^d C_w (μg/l)	^e M_w (μg)	P_b (%)
1	25	12	106	11,554	0.22	1.13	0.249	0.0022
2	35	22	115	12,535	0.37	0.76	0.281	0.0022
3	25	12	768	83,712	0.22	12.0	2.640	0.0032
4	35	22	847	92,323	0.38	7.07	2.687	0.0029

^a Mean benzene vapor concentration.

^b Mass of benzene that passed through the CWFA system during each one-hour sampling period.

^c Mean volume of water produced per test condition.

^d Mean benzene concentration in product water.

^e Mass of benzene in the product water during each one-hour sampling period.

increases, benzene will volatilize into the air and less will be contained in the water.

4. Conclusion

The impact of benzene vapor concentration on the product water quality of CWFA technology was studied in an environmental chamber. This study found that benzene vapor concentrations representing a polluted outdoor environment resulted in benzene product water concentrations between 15% and 23% of the USEPA drinking water limit of 5 μg/l. In contrast, product water benzene concentrations representing an indoor industrial environment were between 1.4 and 2.4 times higher than the drinking water limit. These findings indicate that air and coil temperature as well as air quality should be considered during operation of the CWFA system as untreated product water quality will be affected by both. This study was limited to testing one contaminant (benzene), which may not represent all VOCs or the impact of interactions between multiple VOCs.

Characteristic of what Henry's Law demonstrates, this study found that the air temperature and benzene vapor concentration in the environmental chamber affected the untreated product water quality from a CWFA system. Accordingly, air temperature was related to the concentration of benzene in the product water but the coil temperature was a better predictor of product water benzene concentrations. Similarly, increased benzene vapor concentrations resulted in increased concentrations of benzene in the product water. In contrast to the conceptual similarities, 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 product water when operated in a highly-polluted environment. Product water values always exceeded Henry's Law calculated values based on air and coil temperatures (ranging from 3.6–1.3 times greater) (Supplementary materials, Table SM.4).

Actual coil temperatures below the measured values and direct condensation of benzene onto the coil are potential causes of elevated product water values. Although the air to condensed product water volume ratio indicate that only a small fraction of benzene vapor was directly condensed into the product water, lower condensing (coil) temperatures and/or higher concentrations of benzene vapor may increase the mass of benzene that condenses into the water and increase the health risk of untreated product water. Given additional time for the product water to warm up to the ambient air temperature and reach equilibrium in an untreated water reservoir open to the atmosphere, as may occur in practical applications of this technology, it is anticipated that benzene concentrations will eventually reflect calculated product water values using air temperature. Though, at indoor industrial vapor concentrations, calculated benzene concentration for product water will still exceed the EPA drinking water standard. Efforts to improve the modeling of VOC concentrations for CWFA system product water must consider the effects of direct condensation of the VOC during product water formation on the coil. A conservative approach to water treatment selection should be applied when CWFA system are operated in indoor industrial settings 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.

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Fig. 5. Mean benzene concentration for product and control water samples for conditions (1–4). Calculated values are based on test condition average benzene vapor concentrations and temperature data. The indoor industrial environment scale is an order of magnitude larger than the polluted outdoor environment scale.

necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government.

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Appendix A. Supplementary data

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