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**Determination of Trace Metals, Volatile Organic Compounds, and Other Water Quality Parameters in
WMU Drinking Water**

Tyler Walter

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ABSTRACT

The USEPA creates drinking water maximum contamination levels to support safety in all environments. Inductively coupled plasma-optical emission spectroscopy (ICP-OES), Watersafe® Drinking Water Test kits, and solid phase microextraction with gas chromatography were used to assess the safety of drinking water in three buildings (Davis Hall, the Chemistry Building, and the Dalton Center) on the campus of Western Michigan University. ICP-OES was used to determine the concentration of several trace metals (Cu, Zn, Fe, Mn, Ni, Pb, and As), Watersafe® Drinking Water Test kits were used to determine the concentration of common contaminants and conditions (E. coli, pesticides atrazine and simazine, NO₃⁻/NO₂⁻, total N, Cl, pH, and hardness), and solid phase microextraction with gas chromatography was used to determine the concentration of several volatile organic compounds of concern (toluene, ethylbenzene, total xylene, and chlorobenzene) in the water samples. Most trace metals and common contaminants and conditions were present at levels below primary EPA standards, while some contaminants were above secondary EPA standards. However, the presence of elevated toluene levels in one sample from the Dalton Center suggests that further screening and testing for this contaminant may be warranted.

INTRODUCTION

The most vital molecule to life on earth is water. Safe, clean drinking water has become an even more hotly contested commodity in the world as population increases and water reserves diminish. With increasing populations across the globe comes an increased water footprint for many countries. A country's water footprint is defined as the total amount of water used to meet basic needs for a year, including the water used in the preparation of foods, clothing products, and industry (Pulsipher, 2011). The water footprint in the United States is between 2100-2500 m³/capita/year, which is among the highest in the world. Furthermore, global climate change may also affect water supply. This is especially problematic in particularly vulnerable areas, such as numerous Northern African and Southwest Asian countries. Another increasing challenge is water contamination. In the United States, water contamination is not as severe as in a country like Nigeria, where less than 50% of the population has sustainable access to improved drinking water, but even so there are numerous challenges to maintaining a viable supply of drinking water for the ever growing population (Veregin, 2010).

Drinking water contaminants include toxic trace metals, volatile organic compounds (VOC's), as well as pesticides and bacteria. Fortunately, it is not only possible to measure levels of these contaminants in water supplies, but it is also possible to reduce the contamination, for example through the use of numerous types of filters. For example, common types of filter used for the removal of VOC's from drinking water supplies are activated carbon filters. These filters come in numerous types, such as activated carbon fibers, granules, felts, and woven media, with effectiveness depending on surface area and the chemical of concern (Navarri et al., 2001).

Water supplied to both Western Michigan University and the city of Kalamazoo comes from groundwater sources that flow through the City of Kalamazoo Public Water Supply System, which is the second largest such system in Michigan (Department of Public Service, 2011). In their annual water quality report, the City of Kalamazoo states that water is treated with limited amounts of chlorine, fluoride, and polyphosphate additives. Water is also passed through two purification stages that aid in iron removal. All contaminants tested in this study are also tested regularly by the Michigan Department of Environmental Quality (MDEQ). In the water district that serves Western Michigan University, known as the high pressure district, there are three wells stations (4, 9, and 12). Information is available for trace metals and common secondary standards (T. Spitzner, personal communication, April 10, 2013) as well as volatile organic compounds including common pesticides (T. Spitzner, personal communication,

April 12, 2013) in this water. A detailed list of the average yearly levels of potential contaminants tested in each well is provided in Tables 1 and 2.

Table 1. Michigan Department of Environmental Quality Data for Wells Providing Water to Western Michigan University.

ND = not detected. (T. Spitzner, personal communication, April 10, 2013).

| Michigan Department of Environmental Quality Water Data for Wells Providing Water to Western Michigan University | | | |
|---|-----------------------------|-------------------------|--------------------------|
| Compound | Concentrations (ppb) | | |
| | Station 4 (2008) | Station 9 (2009) | Station 12 (2012) |
| Cu | <20.0 | <20.3 | <22.5 |
| Zn | 414 | <20.0 | <20.0 |
| Fe | 1390 | 528 | 665 |
| Mn | 96.4 | 193 | 63.8 |
| Ni | <20.0 | <20.0 | <20.0 |
| As | <5.00 | <6.18 | 7.75 |
| Pb | <5.50 | <3.00 | <3.00 |
| NO ₃ ⁻ | <100 | <100 | <100 |
| NO ₂ ⁻ | <100 | <100 | <100 |
| pH | 6.95 | 6.72 | 8.11 |
| Hardness | 337 | 368 | 324 |
| | Station 4 (2013) | Station 9 (2013) | Station 12 (2013) |
| Cl | 1.10 ppm | 1.39 ppm | 1.64 ppm |
| Bacteria | ND | ND | ND |

Table 2. Michigan Department of Environmental Quality Data for Wells Providing Water to Western Michigan University.

ND = not detected. (T. Spitzner, personal communication, April 12, 2013).

| Michigan Department of Environmental Quality for Wells Providing Water to Western Michigan University | | | |
|--|------------------------------------|------------------|-------------------|
| Compounds | Concentration in 2012 (ppb) | | |
| | Station 4 | Station 9 | Station 12 |
| Chlorobenzene | <0.5 | <0.5 | <0.5 |
| Ethylbenzene | <0.5 | <0.5 | <0.5 |
| Toluene | <0.5 | <0.5 | <0.5 |
| Total Xylene | <1.5 | <1.5 | <1.5 |
| Atrazine | ND | ND | ND |
| Simazine | ND | ND | ND |

Drinking water contaminants in the United States are regulated by the United States Environmental Protection Agency (USEPA). The EPA has derived standards, secondary standards, and regulatory ranges for many categories of drinking water contamination that have been shown to produce unsatisfactory health risks (Tables 3-5). According to the drinking water contaminant data provided by the USEPA, long-term exposure to any of these contaminants with primary regulation standards can produce adverse health effects. For instance, the chronic ingestion of exceedingly high levels of lead (≥ 15 ppb) can lead to kidney problems and high blood pressure in adults, and an increased risk of slowed mental or physical development in children and infants. Chronic ingestion of toluene in drinking water at levels of 1 ppm or greater have been shown to produce liver, kidney, and nervous system effects. Secondary drinking water standards are set for “nuisance” contaminants that produce skin or tooth discoloration or influence the taste or odor of the water (USEPA, 2009).

Table 3. Maximum contaminant limits set by the EPA for the trace metals Cu, Zn, Fe, Mn, Ni, and As.

Secondary Standards are denoted with an * (USEPA, 2009).

| EPA Maximum Contaminant Limits and Secondary Standards of Various Trace Metals in Drinking Water | |
|---|--------------------------------------|
| Trace Metal | EPA MCL or Secondary Standard |
| Cu | 1 ppm (1000 ppb)* |
| Zn | 5 ppm (5000 ppb)* |
| Fe | 0.3 ppm (300 ppb)* |
| Mn | 0.05 ppm (50 ppb)* |
| Ni | 0.1 ppm (100 ppb) |
| As | 0.01 ppm (10 ppb) |

Table 4. Maximum contaminant levels and guideline standards for the specified contaminants and conditions (City Water Test Kit, 2013).

| EPA Maximum Contaminant Level Drinking Water Standards | |
|---|----------------|
| Contaminant/Condition | EPA MCL |
| Bacteria (<i>E. coli</i>) | None |
| Lead | 15 ppb |
| Pesticides (atrazine/simazine) | 3 ppb atrazine |
| | 4 ppb simazine |
| Total Nitrate/Nitrite | 10 ppm |
| Nitrite | 1 ppm |
| Total Chlorine | 4 ppm |
| pH | 6.5 to 8.5 |
| Total Hardness | 50 ppm |

Table 5. Maximum contaminant levels for toluene, ethylbenzene, total xylene, and chlorobenzene as regulated by the EPA (USEPA, 2009).

| EPA Maximum Contaminant Level Drinking Water Standards for Several VOC's | |
|--|---------|
| Compound | EPA MCL |
| Toluene | 1 ppm |
| Ethylbenzene | 0.7 ppm |
| Total xylene | 10 ppm |
| Chlorobenzene | 0.1 ppm |

A variety of methods are typically used to measure common drinking water contaminants. One of these methods is inductively coupled plasma-optical emission spectroscopy (ICP-OES), also known as inductively coupled plasma-atomic emission spectroscopy (ICP-AES). ICP-OES is a multi-element technique commonly used for trace metal determination (Baysal et al., 2013). Samples are heated to a temperature of 10,000 °C to achieve effective atomization. A plasma source is used to excite the atoms in the sample, causing them to emit light at element-specific wavelengths. Commonly, the ICP torch is radio frequency powered and the wavelength selector is a polychromator (Baysal et al., 2013). The intensity of emitted light is measured via a detector, and calibration standards are used to relate the emission intensity to the concentration of the element in the sample. Two common detectors used in ICP-OES are photomultipliers or charge capacitive discharge arrays (Figure 1).

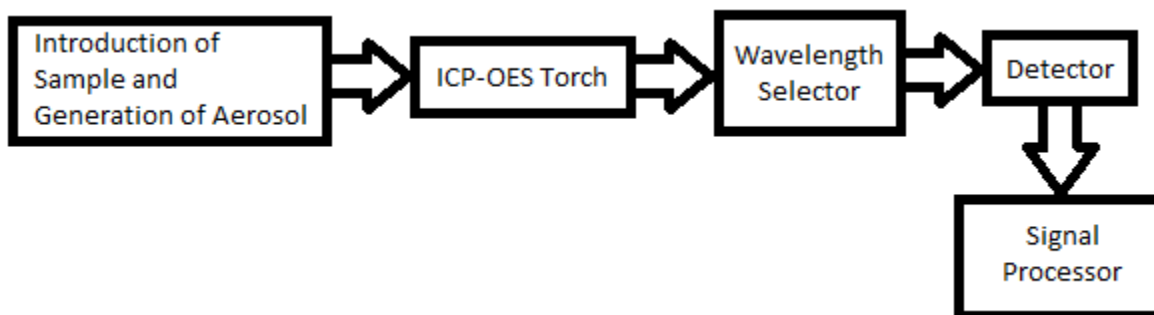


Figure 1. Simple block diagram of the ICP-OES mechanism. Adapted from <http://www.intechopen.com/books/waste-water-treatment-technologies-and-recent-analytical-developments/determination-of-trace-metals-in-waste-water-and-their-removal-processes>, retrieved March 25, 2013.

The plasma configuration of the instrument indirectly affects the detection limits available for analysis. When the plasma source is viewed from the side, it is termed “radial” configuration, while viewing the plasma source from a horizontal vantage is termed “axial” configuration. Axial configuration allows the plasma source to be viewed along its length, which provides the benefit of amplified signal-to-noise, leading to lower detection limits. Axial configuration is commonly used to determine concentration expected to be less than 1000 ppb, while radial configuration is commonly used for expected concentrations above 1000 ppb.

Contamination in drinking water can also be tested using less sophisticated technologies, such as purchasable kits, which can be used to test drinking water for common contaminants and/or unsatisfactory conditions. For example, the Watersafe® Drinking Water Test kit, produced by Silver Lake Research Corporation, can be purchased for \$19.95 on-line (discovertesting.com), or from local stores such as Whole Foods. This product is marketed by the company as a way to support Environmental Protection Agency drinking water standards, improve child safety by reducing lead ingestion, and to aid in the Center for Disease Controls fight against *Escherichia coli* caused illness (City Water Test Kit, 2013).

While simple test kits may provide acceptable data for some contaminants, others require more sophisticated testing methods. For example, volatile organic compounds, such as toluene and chlorobenzene, can be determined by the Solid Phase Microextraction (SPME) method using Gas Chromatography (GC). SPME is a method that has recently been accepted as a viable way to concentrate compounds for very sensitive analysis of various organic compounds (Pecoraino et al., 2008). There are two different types of SPME

procedures: direct, or immersion SPME and headspace SPME.

Direct SPME involves insertion of a SPME fiber directly into the liquid matrix, while headspace SPME is based on absorption of compounds from the vapor above the liquid matrix. The SPME fiber is composed of fused silica, and is

exposed to either the vapor or

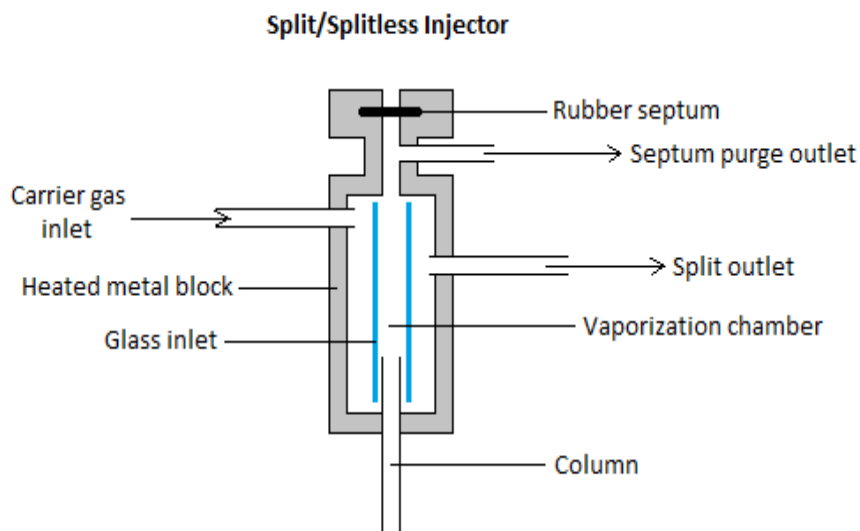


Figure 2. Simple diagram of a split/splitless injector. Adapted from http://lipidlibrary.aocs.org/gc_lipid/03_theor/index.htm, retrieved March 23, 2013.

liquid in order to absorb the target compounds (Pecoraino et al., 2008). Once absorption is complete, the fiber is injected into the inlet of the gas chromatogram. A diagram of an inlet is shown above.

Once the sample is injected into the heated GC inlet, it encounters the carrier gas, which vaporizes it (Christie, 1989). This gas is the mobile phase in this method, and the liquid packed into the gas chromatography column is the stationary phase. The injector may be used in split or splitless mode (Figure 2). As the absorbed compounds from the SPME fiber are desorbed into the gas chromatogram column, they are heated up along a set gradient, which affects the affinity of each compound for the gas or liquid state within the column. As the compounds are eluted from the column, they are combusted in the presence of hydrogen and air and collected by an electrode located directly above the flame that produces a proportional electrical signal measured by a detector. There are various types of detectors; the most widely used is the flame ionization detector (FID). This electrical signal is then amplified, passed to a recorder, and integrated in order to monitor the separation process (Christie, 1989; Figure 3).

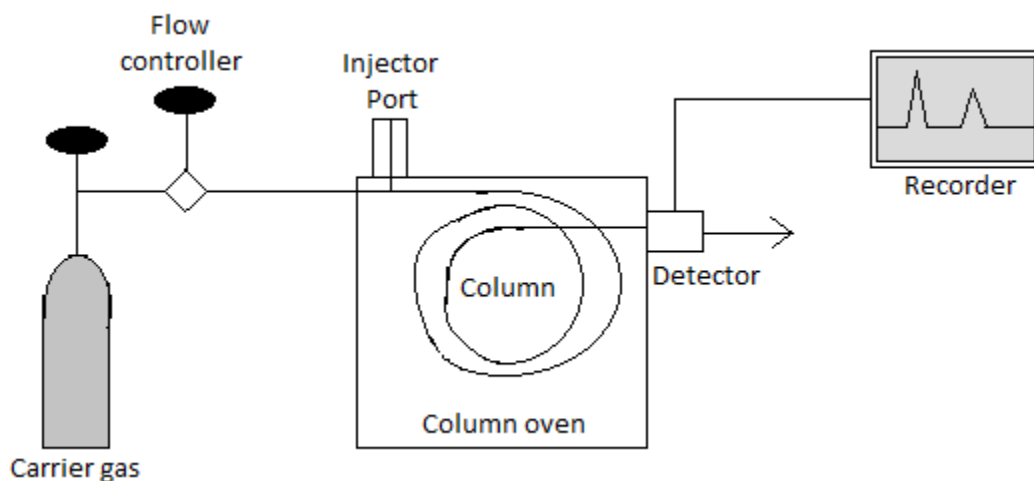


Figure 1. A simple diagram of the overall mechanism of a gas chromatogram. Adapted from <http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrom.htm>, retrieved March 23, 2013.

The four objectives of this study are:

- To determine the concentrations of various trace metals (Cu, Zn, Fe, Mn, Ni, Pb and As) in on campus drinking water sources.

- To determine average hardness, pH, *Escherichia coli* levels, and concentrations of select pesticides (atrazine/simazine), $\text{NO}_3^-/\text{NO}_2^-$, NO_2^- (as N), and Cl in the same drinking water samples tested for trace metals.
- To determine the concentrations of a suite of volatile organic compounds (toluene, ethylbenzene, xylene, and chlorobenzene) in the same drinking water samples tested for trace metals.
- To compare the contaminant concentrations among select buildings on campus in order to determine the influence of building age and water source distance from the buildings water supply entrance on contaminant levels, and to compare measured concentrations to EPA standards for these chemical species.

It is hypothesized that the concentrations of trace metals, volatile organic compounds, pesticides, nitrate, nitrite, and chlorine will increase with increasing distance of the water source from the initial water supply entrance point into the building due to longer exposure to the pipes that distribute potable water and their accumulated contaminants. Also, it is hypothesized that concentrations of these chemical species will increase with the increased age of the specific buildings due to increased time to accumulate contaminants and experience deterioration. Lastly, it is hypothesized that the levels of hardness, pH, and bacteria will not be affected by the distance from the initial water supply, but will depend solely on the age of the specific building being analyzed.

METHODS

Sample Collection

Samples for ICP-OES analyses were collected in acid-washed, 20 mL polyvinyl vials that were filled with ultrapure water until use. Approximately 1 mL of water was collected at each water source for SPME analyses. These samples were directly collected in the vials to be used for these analyses and the caps screwed on tightly. Water samples were collected from drinking fountains and faucets in Davis Hall, the Chemistry Building, and the Dalton Center. Gloves were worn for all sample collections.

Samples for ICP-OES from Davis Hall were taken from a drinking fountain on the ground floor, a faucet in a first floor dorm room (in duplicate), a faucet in the second floor lounge, and a faucet in a third floor dorm room (in duplicate). Samples for ICP-OES from the Chemistry Building were taken from

the drinking fountains located on the first, second, and third floors with the first and third floors having duplicates. Samples for ICP-OES from the Dalton Center were collected from a first floor drinking fountain at the northeast end of the building, a first floor drinking fountain near the southeast end of the building, and a second floor drinking fountain located near the northeast end of the building (in duplicate). Samples for ICP-OES were taken from Davis Hall and the Dalton Center on November 11th of 2012, while samples were collected from the Chemistry Building on November 13th. During collection, drinking fountains and faucets were allowed to run for 3-5 seconds before collection and samples were immediately acidified with 2-3 drops of 5% nitric acid. Water blanks were collected in each building (one per building) by opening up the vial, waving it around to collect anything residually found in the air environment of the building, adding 2-3 drops of 5% nitric acid, and then storing with the rest of the collected water samples in a refrigerator.

Water samples used for the Watersafe Drinking Water tests were tested immediately after collection. Samples used from the ground floor of Davis Hall and both samples from the first and third floors of the Chemistry Building were collected on February 19th of 2013. The samples from the first floor of Davis Hall were collected on February 20th, and both samples from the first and second floors of the Dalton Center were collected on March 22nd.

Finally, water samples for SPME analyses were collected using the same sources as for the ICP-OES water samples, except that no duplicates were collected. First, a sample was taken from the third floor of Davis Hall dorm room faucet, the same used for the ICP-OES water samples, on March 18th of 2013. All water samples from the Chemistry Building (first, second, and third floors) and two samples from the Dalton Center (first floor SE and second floor NE) were collected on March 20th, while the remaining samples from the Dalton Center (first floor NE) and all remaining samples from Davis Hall (ground floor, first floor, and second floor) were collected on March 22nd. Explanation for notations used in following data tables is shown below (Table 6).

Table 6. Notation explanations for all data tables.

| Explanation for ICP-OES Data Notations | |
|--|---|
| Notation Used | Explanation |
| “Control” | Water source closest to water inlet into building |
| “#” or “ground” | Number after building indicates floor, “ground” means ground floor |
| “a” or “b” | Duplicates collected at the same water source, with “a” representing the first sample collected, and “b” representing the duplicate sample. |

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Analysis of Trace Metals

Multi-element calibration standards (0, 25, 50, 100, 250, 500, and 1000 ppb of Cu, Zn, Fe, Mn, Ni, and As) were mixed from a stock standard solution. An yttrium internal standard was added to each calibration standard and sample. Standards were prepared to a final volume of 50 mL, consisting of 50 µL of 1000 ppm yttrium, a calculated amount of each trace metal stock solutions, 3.57 mL of 5% nitric acid, and diluted to the remaining volume with ultrapure water. Because two different trace metal stock solutions (one containing Cu, Zn, Fe, Mn, and Ni and the other containing As) were used to make the standards, a calculated amount of each solution was added to each standard.

Water samples were also prepared for analysis using an yttrium internal standard. The samples were prepared to a final volume of 10 mL, with each solution containing 8 mL of the specified water sample, 714 µL of 5% nitric acid, 10 µL of 1000 ppm yttrium, and diluted to the remaining volume with 1.276 mL of ultrapure water.

Calibration standards were analyzed using a Perkin Elmer ICP-OES Optima 2100 DV operating in axial mode, with a linear working range up to 1000 ppb. Data acquisition and analysis was completed using WinLab32 ICP operating software. The calibration standards required an r^2 value of at least 0.9999 in order to present a satisfactory calibration curve. All of the standards exhibited this level of accuracy except for Zn, which displayed an r^2 value of roughly 0.9998.

The water samples were also run in axial mode, with concentrations of each analyte calculated based on the pre-established calibration curves. Each sample was analyzed in triplicate, resulting in standard deviation of <5%, except when analytes were below the instrument detection limits. The yttrium internal standard was also used as a quality assurance/quality control. Negative reported concentrations and concentrations with an RSD <5% were reported as below detection limits (BDL). In

order to calculate the actual concentration for the water samples tested, the raw data concentration acquired from the ICP software were corrected for sample dilution prior to analysis (Tables 7-9). An example of this calculation is shown below.

$$(\text{observed concentration})(\text{total volume}) = (\text{volume of water sample})(\text{actual concentration})$$

$$(419.200 \text{ ppm})(10 \text{ mL}) = (8 \text{ mL}) \times n \qquad n = \frac{(10 \text{ mL} \times 419.2 \text{ ppm})}{8 \text{ mL}} = 524 \text{ ppm}$$

Watersafe® Drinking Water Test Kit Analysis of Drinking Water

All procedures closely follow the methods and precautions described in the Watersafe drinking water test kit directions manual.

The supplied bacteria test vial was set upright on a flat surface. After the temperature of the drinking water was tested using a digital thermometer, the water was collected in the vial by carefully removing the cap, adding the water up to the 5 mL line, and replacing the cap tightly. Once capped, the vial was shaken for roughly 20 seconds on site, placed upright in room temperature (25°C), and left undisturbed for 48 hours. After this incubation period, the results were indicated by a color change with a purple solution indicating a negative result, and a yellow solution indicating a positive result. Samples with positive results, indicating the presence of any *Escherichia coli* were disposed of by adding bleach before disposal while those with negative results were simply flushed down a toilet.

The lead/pesticides (atrazine/simazine) packet was opened on site and its contents were removed. Using the supplied dropper, exactly two dropperfuls of water sample was placed in the supplied vial, which was then swirled gently for roughly 5 seconds, and subsequently placed on a flat surface on site. Both the lead and pesticide test strips were placed into the test vial with the arrows pointing down and left undisturbed for 10 min. After this period of time, the strips were analyzed by viewing the lines developed between the 1 and 2 positions on each strip. The presence of a darker line near 1 indicates a negative test while a darker line near 2 indicates a negative test, meaning the lead or pesticides levels may be above the established EPA drinking water standards of 15 ppb for lead, 3 ppb for atrazine, and 4 ppb for simazine.

The nitrate/nitrite packet was opened and its contents were removed on site. The reagent pad containing a test pad for both nitrate and nitrite was exposed to the water sample for roughly 2 sec and then left undisturbed for 1 min. After this period of time, the test pads were compared against the provided color charts for both nitrate/nitrite and nitrite (as N). Tests that presented results above the

designated concentration on the color chart may be over the established EPA drinking water standards set for nitrate/nitrite of 10 ppm and nitrite (as N) of 1 ppm.

The pH/hardness/chlorine packet was opened and its contents were removed on site. The reagent pad containing a pH indicator pad, a hardness indicator pad, and a total chlorine indicator pad was dipped into the water sample and removed immediately. The strip was held level for roughly 15 sec before each pad was analyzed against the provided color charts for pH, hardness, and total chlorine. Tests that presented results above the designated concentration on the color chart may be over the established EPA drinking water standards set for pH at a range of 6.5 to 8.5, hardness at 50 ppm, and total chlorine at 4 ppm.

Gas Chromatography Analysis of Volatile Organic Compounds Using Headspace SPME

A 20 ppm stock solution of toluene (99.97% purity) was prepared by introducing 1.154 μL of pure toluene into a 50 mL volumetric flask and diluting to a volume of 50 mL with milli-Q water. From this stock solution, 5 mL was placed in a new 50 mL volumetric flask and diluted to a volume of 50 mL with deionized water, creating a 2 ppm toluene stock solution. Finally, from the 2 ppm solution, 5 mL was placed in a new 50 mL volumetric flask and diluted with milli-Q water, creating a 0.2 toluene ppm solution. This serial dilution method was also used to create calibration standards for xylene and ethylbenzene. The only difference being that 1.157 μL of the pure xylene mixture ($\geq 98.5\%$ purity) in ethylbenzene was added to the initial stock solution. Because the densities of the xylene mixture and ethylbenzene are nearly identical, the calibrations used for total xylene were also used for determining ethylbenzene calibration standards.

The method used for toluene and xylene is similar to the method used for creating the chlorobenzene calibration standards, save some key differences. First, 1.130 μL of pure chlorobenzene (100% purity) was added to the initial stock solution to create a 25 ppm stock solution. This stock solution was used to create the 2.5 ppm solution, and this solution was then used to create the 0.25 ppm solution using the same dilution ratios (1:9) used in the preparation of the toluene and xylene standards. However, the 0.25 ppm solution was diluted down further to a 0.05 ppm solution by adding 10 mL of the 0.25 ppm solution to a 50 mL volumetric flask and diluting to a volume of 50 mL with milli-Q water.

Once standards were prepared, approximately 1 mL of each solution was placed in a clean vial to which a magnetic stir bar was added. The cap, with a neoprene center for SPME fiber insertion, was screwed on tightly and the vial was labeled accordingly and placed in its respective slot on the GC tray.

First, each vial was placed in a 40°C thermostated bath for 5 min, with agitation, before the 85 µm Carboxen®/polydimethylsiloxane SPME fiber (Supelco Inc.) was placed in the vial and allowed to absorb the gaseous vapors within the headspace of the vial for 20 min. After this time period, the fiber was placed into the injector, which was set to a temperature of 250°C, and allowed to desorb into the GC column for 5 minutes before the fiber was extracted. The GC column (Supelco Inc.) was 30 m long, internally coated with a 0.32 mm I.D., and support that was 1.5 µm thick, with a maximum temperature of 260°C. The GC column temperature program was initially at 40°C where it remained for 2 min before temperature programmed at 8°C/min until reaching a temperature of 210°C. The carrier gas used for this experiment was helium with a flow rate of 50.8 mL/min and an average velocity of 29 cm/s while in splitless mode. Overall, the approximate time for one sample to run is 50 minutes. The method described above was created loosely following the similar design used by Pecoraino *et al.* (2008).

Each set of calibration standards was run a minimum of 3 times in order to determine the average area for the respective peak of each analyte. Once these averages were determined, this area was plotted against the known concentrations of the standards to create a working calibration curve and determine its slope. Also, error bars were created for each point on the calibration curve to determine the expected error in sample analyses.

The caps of SPME vials used to collect water samples (see above) were each unscrewed, a magnetic stir bar placed inside, and the cap was replaced on each vial. The vial was then labeled accordingly and placed in the GC auto sampler. Each water sample was run twice in order to account for the possibility of unexplained contamination during one trial and to observe the effect that time spent in the vial at room temperature over the course of a weekend had on the sample. Detected peaks were analyzed using the slope-intercept equation produced by the calibration curve and the observed peak area, in order to calculate the concentration of each analyte in each water sample. An example of this analysis is shown below.

$$y = mx + b \qquad x = \frac{(y-b)}{m} \qquad x = \frac{(0.52-0.2261)}{0.2636} = 1.115 \text{ ppm toluene}$$

RESULTS

Determination of Metals (Cu, Zn, Fe, Mn, Ni, and As) in Drinking Water by ICP-OES

All analyzed building water samples showed measurable concentrations of the trace metals determined, with numerous concentrations above EPA limits. The data used for further discussion were the results exhibited without considering any contribution from yttrium as this data produced lower relative standard deviations (RSD) compared to the data produced when considering yttrium contributions. Data from each building is provided below (Tables 7-9).

Table 7. Trace metal concentrations in water samples from Davis Hall.

BDL= below detection limits. Values in bold are above EPA limits.

| Trace Metal Concentrations in Drinking Water from Davis Hall | | | | | | |
|---|---|-------------|-----------|-----------|-----------|-----------|
| Location | Trace Metal Concentration (in ppb) | | | | | |
| | Fe | Mn | Cu | As | Zn | Ni |
| Davis blank | BDL | 0.52 | 8.2 | BDL | BDL | BDL |
| Davis control | 712 | 60.7 | 20.9 | BDL | 2350 | BDL |
| Davis 1a | 476 | 52.8 | 17.8 | BDL | 360 | BDL |
| Davis 1b | 406 | 58.3 | 7.4 | BDL | 215 | BDL |
| Davis 2 | 478 | 23.7 | 6.7 | BDL | 2530 | 8.2 |
| Davis 3a | 336 | 49.5 | BDL | BDL | 379 | BDL |
| Davis 3b | 342 | 48.6 | BDL | BDL | 301 | BDL |

Table 8. Trace metal concentrations in water samples from the Chemistry building.

BDL = below detection limits. Values in bold are above EPA limits.

| Trace Metal Concentrations in Drinking Water from the Chemistry building | | | | | | |
|--|------------------------------------|------|-------------|-----|------|-----|
| Location | Trace Metal Concentration (in ppb) | | | | | |
| | Fe | Mn | Cu | As | Zn | Ni |
| Chem blank | BDL | 0.47 | BDL | BDL | BDL | BDL |
| Chem control a | 208 | 42.7 | 400 | BDL | BDL | BDL |
| Chem control b | 213 | 42.0 | 390 | BDL | BDL | BDL |
| Chem 2 | 353 | 49.1 | 1010 | BDL | 23.3 | BDL |
| Chem 3a | 276 | 38.3 | 472 | BDL | BDL | BDL |
| Chem 3b | 275 | 38.0 | 474 | BDL | BDL | BDL |

Table 9. Trace metal concentrations in water samples from the Dalton Center.

BDL=below detection limits. Values in bold are above EPA limits.

| Trace Metal Concentrations in Drinking Water from the Dalton Center | | | | | | |
|---|------------------------------------|------------|-----|-----|------|-----|
| Location | Trace Metal Concentration (in ppb) | | | | | |
| | Fe | Mn | Cu | As | Zn | Ni |
| Dalton blank | BDL | 0.39 | 4.5 | BDL | BDL | BDL |
| Dalton control | 2720 | 226 | 347 | 4.5 | 196 | BDL |
| Dalton 1 (SE) | 524 | 47.2 | 722 | BDL | 383 | BDL |
| Dalton 2a (NE) | 1240 | 111 | 626 | BDL | 36.3 | BDL |
| Dalton 2b (NE) | 1590 | 142 | 637 | BDL | 39.4 | BDL |

Watersafe® Drinking Water Tests

All analyzed water sources within the various buildings tested yielded acceptable results for almost every test in the kits. Water temperature and test results are presented below (Table 10).

Table 10. Results for Davis Hall, the Chemistry Building, and the Dalton Center from the Watersafe® Drinking Water Tests.

† denotes a lead test that presented data too close to distinguish between positive and negative results.

* denotes data entries near or at the EPA limit. Bolded data entries denote concentrations above the EPA limit.

| Watersafe® Drinking Water Tests | | | | | | | | | |
|---------------------------------|-------------------|----------|-----------------|-----|-----------------|---|----------------------|----------------|---|
| Location | Water Temperature | Bacteria | Lead/Pesticides | | Nitrate/Nitrite | | pH/Hardness/Chlorine | | |
| Davis Ground | 23.2 °C | (-) | (-) | (-) | 0 | 0 | 8.5* | 425 | 0 |
| Davis 1 st Floor | 13.4 °C | (-) | (+/-)† | (-) | 0 | 0 | 7.5 | 250-425 | 0 |
| Chem 1 st Floor | 11.7 °C | (-) | (-) | (-) | 0 | 0 | 7.5-8.5* | 250-425 | 0 |
| Chem 3 rd Floor | 12.3 °C | (-) | (-) | (-) | 0 | 0 | 7.5 | 250 | 0 |
| Dalton 1 st Floor | 10.3 °C | (-) | (-) | (-) | 0 | 0 | 7.5 | 250 | 0 |
| Dalton 2 nd Floor | 10.4 °C | (-) | (-) | (-) | 0 | 0 | 7.5-8.5* | 250-425 | 0 |

SPME Determination of Volatile Organic Compounds

Calibration standards were analyzed and results were output from the GC operating software. Retention times determined using pure vials of each analyte (Table 11).

Table 11. Retention times relative to unretained peaks for toluene, ethylbenzene, all forms of xylene, and chlorobenzene as determined by GC analysis.

| Retention Times for VOC's | |
|----------------------------------|------------------------------|
| Compound | Retention Times (min) |
| Toluene | 4.53-4.58 |
| Ethylbenzene | 5.87-5.950 |
| Total xylene | 6.03-6.10 (p-xylene) |
| | 6.14-6.24 (m-xylene) |
| | 6.90-6.95 (o-xylene) |
| Chlorobenzene | 7.42-7.43 |

The retention times shown in Table 11 were used to identify the peaks corresponding to each analyte. Calibration data, including relative peak area for three replicates and associated standard deviations are shown in Tables 12-15.

Table 12. Results of toluene calibration standard GC analysis, including the mean (average) and the sample standard deviation.

| Toluene Calibration Data | | | | | |
|---------------------------------|---------------|---------------|---------------|----------------|---------------------------|
| Concentration | Area | | | | |
| | Run #1 | Run #2 | Run #3 | Average | Standard Deviation |
| 0.2 ppm | 0.270 | 0.300 | 0.330 | 0.300 | 0.030 |
| 2 ppm | 1.100 | 0.470 | 0.620 | 0.730 | 0.329 |
| 20 ppm | 5.500 | 2.600 | 10.400 | 5.500 | 2.900 |

Table 13. Results of ethylbenzene calibration standard GC analysis, including the mean (average) and the sample standard deviation.

| Ethylbenzene Calibration Data | | | | | |
|--------------------------------------|---------------|---------------|---------------|----------------|---------------------------|
| Concentration | Area | | | | |
| | Run #1 | Run #2 | Run #3 | Average | Standard Deviation |
| 0.2 ppm | 0.440 | 0.230 | 0.240 | 0.303 | 0.118 |
| 2 ppm | 0.800 | 0.190 | 0.320 | 0.437 | 0.321 |
| 20 ppm | 4.100 | 5.300 | 7.800 | 5.733 | 1.888 |

Table 14. Results of total xylene calibration standard GC analysis, including the mean (average) and the sample standard deviation.

| Total Xylene Calibration Data | | | | | |
|--------------------------------------|---------------|---------------|---------------|----------------|---------------------------|
| Concentration | Area | | | | |
| | Run #1 | Run #2 | Run #3 | Average | Standard Deviation |
| 0.2 ppm | 2.720 | 1.350 | 1.600 | 1.890 | 0.730 |
| 2 ppm | 6.100 | 1.150 | 2.560 | 3.270 | 2.550 |
| 20 ppm | 28.400 | 35.900 | 51.600 | 38.633 | 11.839 |

Table 15. Results of chlorobenzene calibration standard GC analysis, including the mean (average) and the sample standard deviation.

| Chlorobenzene Calibration Data | | | | | |
|---------------------------------------|---------------|---------------|---------------|----------------|---------------------------|
| Concentration | Area | | | | |
| | Run #1 | Run #2 | Run #3 | Average | Standard Deviation |
| 0.05 ppm | 0.760 | 0.260 | 0.300 | 0.440 | 0.278 |
| 0.25 ppm | 0.370 | 1.200 | 1.200 | 0.923 | 0.479 |
| 2.5 ppm | 1.800 | 0.520 | 3.100 | 1.807 | 1.290 |
| 25 ppm | 25.000 | 9.100 | 4.500 | 12.867 | 10.757 |

The data shown in Tables 12-15 were used to create working calibration curves for each analyte. The standard deviation was used to approximate errors (Figures 4-7).

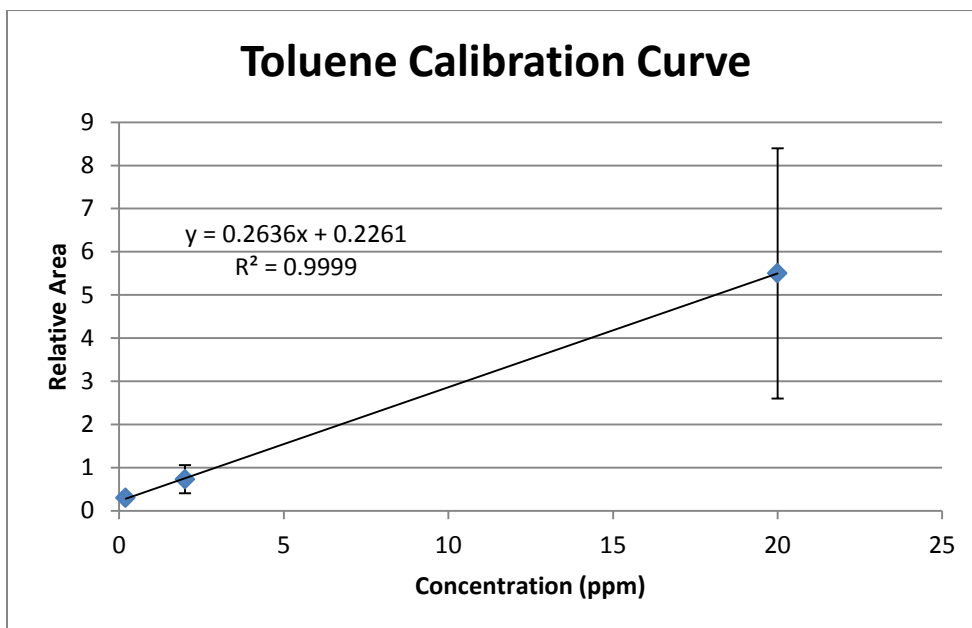


Figure 4. Calibration curve, with standard deviation error bars, for the GC analysis of toluene.

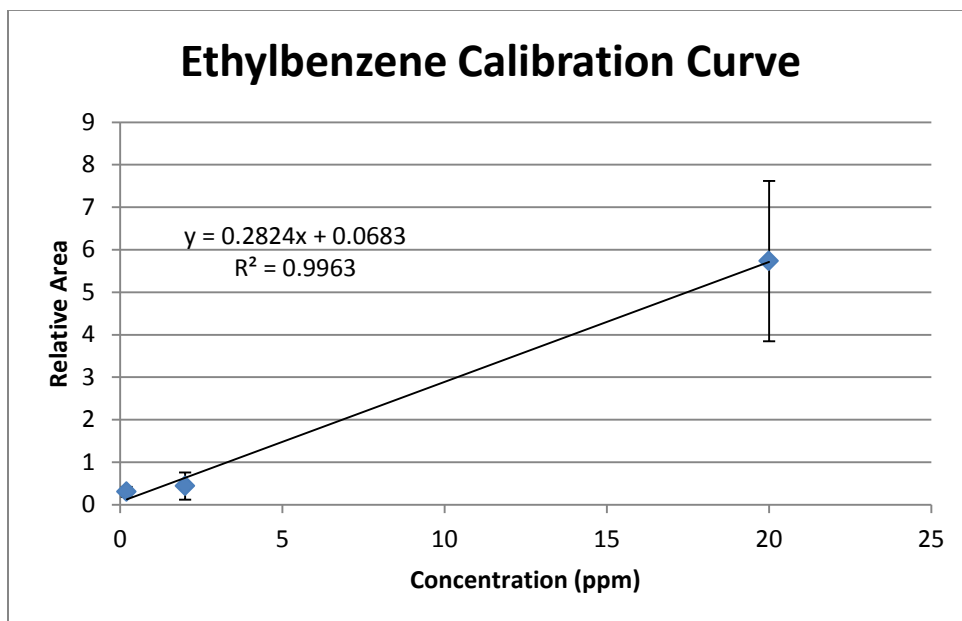


Figure 5. Calibration curve, with standard deviation error bars, for the GC analysis of ethylbenzene.

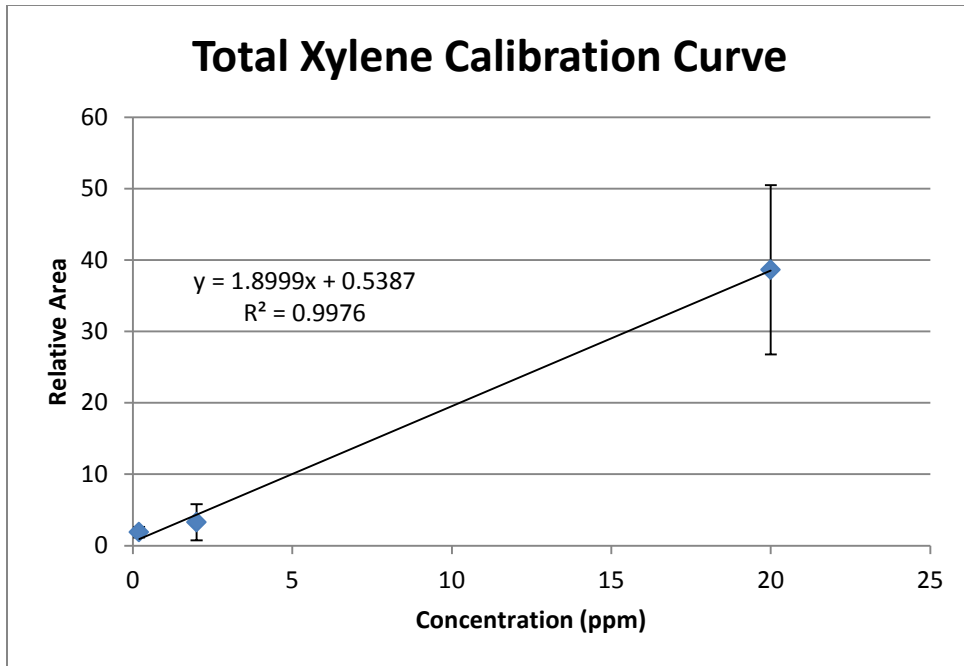


Figure 6. Calibration curve, with standard deviation error bars, for the GC analysis of toluene.

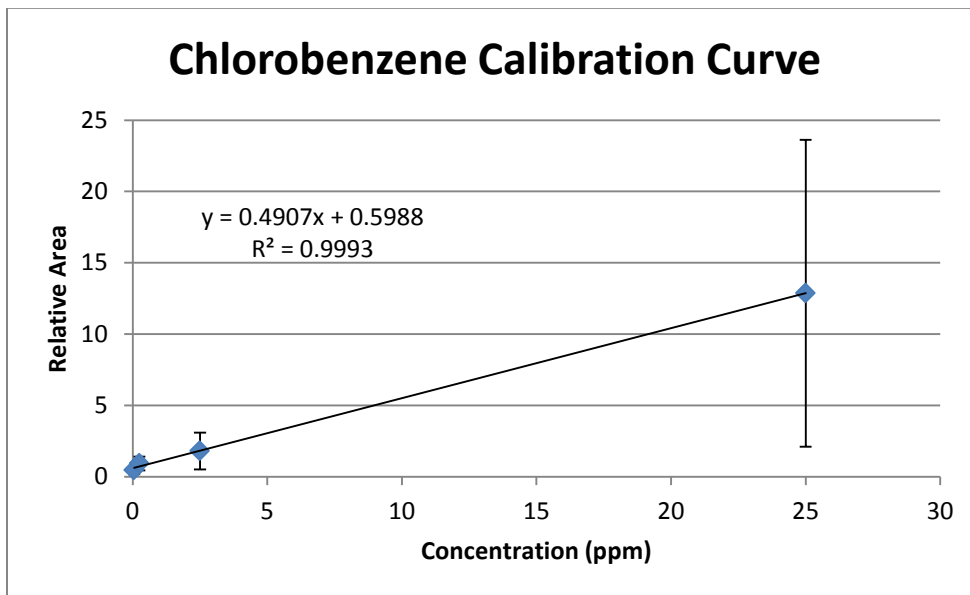


Figure 7. Calibration curve, with standard deviation error bars, for the GC analysis of toluene

Finally, water samples from each water source were analyzed in replicate and concentrations of each analyte calculated using the calibration data shown in Fig 4-7 (Table 16).

Table 16. Results of GC analysis for both trials of all water samples from Davis Hall, the Chemistry Building, and the Dalton Center. Data entries that state "below a given value" represent the absence of peaks, indicating that results are below detection limits determined for each compound. * denotes a detected peak that was calculated to be below detection limits. Bolded data entries represent concentrations above the EPA limit for that compound.

| Water Sample Analysis Data | | | | | | | | |
|----------------------------|-----------------------------|--------------|--------------|--------------|--------------|--------------|---------------|---------------|
| Water Source | Analyte Concentration (ppm) | | | | | | | |
| | Toluene | | Ethylbenzene | | Total Xylene | | Chlorobenzene | |
| | Trial 1 | Trial 2 | Trial 1 | Trial 2 | Trial 1 | Trial 2 | Trial 1 | Trial 2 |
| Davis Ground | detected, below 0.2* | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Davis 1 | detected, below 0.2* | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Davis 2 | detected, 0.622 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Davis 3 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Dalton 1 NE | detected, 1.1 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Dalton 1 SE | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Dalton 2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Chem 1 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Chem 2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |
| Chem 3 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.2 | below 0.05 | below 0.05 |

DISCUSSION

The pipes used for potable drinking water in most of the buildings found on campus are a mixture of galvanized, copper, and plastic piping. Also, all pipes on the campus of WMU follow American Society of Mechanical Engineers (ASME) Standards provided for potable plumbing pipe specifications such as pressure, joints, and other mechanical issues. Based on specifications provided by the American Society for Testing and Materials (ASTM) designations B88 – 09 and A53/A53M – 12, the galvanized pipe contains, Fe, C, Mn, P, S, Cu, Ni, Cr, Mo, V, and the Zn-coating used to galvanize the pipe. The copper pipe used contains Cu (with Au) and trace amounts of P (ASTM, 2009; ASTM, 2012). Plastic piping is commonly made from chlorinated polyvinyl chloride, or CPVC pipe, usually with a schedule 40 rating. While there are slight differences in the concentrations of compounds in the piping between ASME and ASTM standards, the overall chemical makeup of the piping varies relatively little, thus it can be assumed that campus piping will contain elements in the ASTM specifications. These data suggest that pipes in all three of the buildings analyzed likely contain Fe, Mn, Cu, Zn, and Ni. Thus, concentrations of these elements might increase in drinking water after prolonged contact with the pipes. Building age may also play an important role in Zn concentrations found in drinking water. Older buildings are assumed to have undergone more corrosion of galvanized piping, leading to increased levels of Zn in drinking water.

Some obvious and more subtle trends are apparent in the trace metal data collected for water from each building (Tables 7-9). First, Fe, Mn, and Cu concentrations in the drinking water of Davis Hall (Table 7) are inversely correlated to distance from the control source, in contradiction of the original hypothesis. The Zn data contains too many outliers to identify any clear trends in concentration with distance from the source water. As and Ni are typically below detection limits in the drinking water. Interestingly, the levels of Fe and Mn found in numerous water samples from Davis Hall exhibited values above the EPA secondary standards (Tables 3 and 7), which can have negative effects on the odor and taste of the water, as well possible staining effects (USEPA, 2009). However, this can be accounted for from the MDEQ data provided for the WMU drinking water source (Table 1).

The trends in concentrations observed in the Chemistry Building (Table 8) generally support the original hypothesis. Fe and Cu concentrations increase with distance from the initial source, suggesting that more contamination with these constituents occurs the longer the water travels through the pipes. However, Mn concentrations shows the opposite trend, decreasing with distance and Ni levels are consistently below detection limits, and Zn concentrations do not present any consistent changes with

distance, as observed for Davis Hall. Similar to Davis Hall, two water samples from the Chemistry Building had Fe and Cu levels above secondary EPA standards (Tables 3 and 8). The MDEQ data explains the high levels of Fe (Table 1), but the high level of Cu could possibly be from copper piping near the drinking water outlet, as some water fountains located on campus have Cu refrigeration pipes.

Trends in trace metal concentrations with distance in the Dalton Center (Table 9) are not as obvious as in Davis Hall or the Chemistry Building. Cu levels increased with distance from the initial source and Zn levels decreased with distance. There is a slight negative trend for Fe and Mn concentrations with distance from the source, compared to the control data, but it does not appear to be significant. Finally, similar to Davis Hall and the Chemistry Building, As and Ni levels were consistently below detection limits. Also, as in Davis Hall, the observed values for Fe and Mn are above the EPA secondary standards (Tables 3 and 9), but can be explained by referencing the MDEQ data for WMU (Table 1).

Davis Hall produced the highest Zn readings, followed by the Dalton Center and then the Chemistry Building, which also happens to be the order for decreasing age of the buildings analyzed, as mentioned above (Tables 7-9). This leads to the conclusion that slightly more corrosion may have occurred over time to the galvanized piping located in Davis Hall as compared to the others.

Further analysis of the drinking water in the three buildings of interest was performed using Watersafe® Drinking Water Test kits. Tests for bacteria, lead, pesticides, nitrate/nitrite, and nitrite produced either negative or null results (Table 10), with the exception of one lead test taken from a first floor dorm room in Davis Hall, which after the 10 min wait period, produced dark blue lines near both 1 and 2. Although the blue line near 2 initially appeared darker, upon closer observation the two lines could not be readily distinguished. These results, except for the unique Pb test result mentioned above, were expected based on the MDEQ data for WMU water sources (Table 1 and 2). Lack of another testing kit precluded further testing for this site that exhibited this ambiguous result. More Pb testing is warranted because the implications of detected Pb concentrations above the EPA limit (Table 4) include serious health effects, for example, kidney problems and high blood pressure, in adults, and far worse health effects for pregnant women and children. The absence of detectable chlorine in any of the drinking water samples refuted the initial hypothesis, but was expected from the MDEQ data (Table 1). There was no significant correlation between hardness levels and the age of the buildings analyzed. However, the hardness values in every water source tested produced values well above the recommended EPA standards of 50 ppm, which do not present bodily harm, but may produce scale

build-up in pipes (USEPA, 2009). Also, the pH of water tested in all three buildings was somewhat alkaline, with the drinking fountain on the ground floor of Davis Hall producing a pH of 8.5, which is the upper boundary of the EPA secondary standard range. However, the EPA regulations for pH are also secondary standards, which may affect the odor and taste of the water, as well as contribute to pipe corrosion, staining, and scale production. Also, a high hardness level and alkaline pH were expected from the data provided by the MDEQ (Table 1).

SPME and gas chromatography was used to determine the concentrations of several volatile organic compounds (toluene, ethylbenzene, total xylene, and chlorobenzene) in the same drinking water samples tested for trace metals, pH, hardness, bacteria, chlorine, and nitrate/nitrite levels. Initially, the chemical of concern was chloroform, but the calibration standards prepared for this compound were below detection limits of roughly 1 ppm, not allowing for any inferences to be made regarding the EPA MCL regulations for drinking water. However, the use of chloroform initially allowed for method development in order to yield the lowest detection limits, allowed for better preparation of calibration standards through simple trial and error, and displayed the effects of dissipation from the vials over time.

The final VOC levels were below detection limits for most of the water samples analyzed (Table 5), but there were a handful of samples with detectable amounts of toluene (Table 16). The toluene concentration was slightly above the EPA standard in one of the two replicate tests of a water sample taken from the drinking fountain at the northeast end of the first floor of the Dalton Center. Although a second analysis of this water sample did not produce any distinguishable peaks for toluene, the first measurement indicates that toluene contamination could be an issue. Furthermore, the first measurement was made using a fresh sample (only an hour old), whereas the second measurement was made with the same samples after exposure to the open atmosphere at room temperature in a vial with a punctured cap. It is possible that evaporative loss of toluene occurred during this period. Toluene concentrations above 1 ppm could potentially result in nervous system, liver, or kidney problems, indicating that further testing of this source is warranted. This result is particularly interesting, as the MDEQ toluene data for WMU showed very low concentrations at all three stations (Table 2), contradictory to the ambiguous result.

CONCLUSIONS

The concentrations of various trace metals, volatile organic compounds, and other chemical substances or conditions showed some correlation with distance from initial entrance into the three buildings analyzed within the context of this experiment. However, most of these correlations showed a negative correlation of concentration with distance from the initial water entrance. This counters the original hypothesis that a positive correlation would be exhibited. Based on the age of the three buildings analyzed, it appears that the only contaminant that showed obvious increased concentration with increased age of the building being analyzed is zinc, which could be explained by slightly more corrosion over time of the galvanized piping. Apart from this trend attributed to age, there were no other correlations associated with the age of the buildings.

The ICP-OES analyses demonstrated that several elements (Fe, Mn, and Cu) were above EPA MCL secondary standards for some cosmetic and aesthetic effects, but most of the element concentrations were below EPA limits. This is also the case for the Watersafe® Drinking Water Tests, which only showed elevated levels of hardness throughout the campus water sources, which is expected from the MDEQ data for water sources to WMU. However, one trial run of the drinking water from the drinking fountain located at the northeast end of the Dalton Center on the 1st floor exhibited a toluene concentration of 1.1 ppm, which is slightly above the EPA limit, warranting further testing. While no toluene peak was observed in a subsequent analysis of the sample, evaporation over time from the vial may have caused the toluene to escape.

Further analysis of the trace metals analyzed by ICP-OES may be better studied by including the consideration of the temperature of the water sample when it was originally collected. This may also improve the study of volatile organic compounds. The use of Watersafe Drinking Water Test kits is largely based upon comparisons performed by one person; these tests should be done with another peer to reduce bias in color chart comparisons. Lastly, both calibration standards and water samples should either be freshly made for each trial, or a non-punctured cap should be placed on the vial in-between trials so as to prevent dissipation and escape of the vapor matrix.

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