

Fall 2015

Predicting Air Concentration from Source Concentrations: An Evaluation of Benzene Emissions from a Benzene Hazardous Waste Stream

Steven Hynek

Montana Tech of the University of Montana

Follow this and additional works at: http://digitalcommons.mtech.edu/grad_rsch



Part of the [Occupational Health and Industrial Hygiene Commons](#)

Recommended Citation

Hynek, Steven, "Predicting Air Concentration from Source Concentrations: An Evaluation of Benzene Emissions from a Benzene Hazardous Waste Stream" (2015). *Graduate Theses & Non-Theses*. 52.
http://digitalcommons.mtech.edu/grad_rsch/52

This Non-Thesis Project is brought to you for free and open access by the Student Scholarship at Digital Commons @ Montana Tech. It has been accepted for inclusion in Graduate Theses & Non-Theses by an authorized administrator of Digital Commons @ Montana Tech. For more information, please contact sjuskiewicz@mtech.edu.

Predicting Air Concentration from Source Concentrations: An Evaluation of
Benzene Emissions from a Benzene Hazardous Waste Stream

By
Steven Hynek, MBA

A report submitted in partial fulfillment of the
requirements for the degree of

Master of Science
Industrial Hygiene Distance Learning / Professional Track

Montana Tech of the University of Montana
2015

Abstract

Benzene is a common chemical in hazardous waste streams. Benzene contaminated wastes may come in the form of a liquid, solid, or sludge. The amount of benzene seen in waste streams depends upon the generator. The generator in this study has a steady supply of benzene wastes. The waste stream has the same consistency as waste streams from other generators; however there is variability in the concentration of benzene. As a result due to the lack of a consistent concentration, additional respiratory protection is in use to mitigate any additional risk from benzene. The waste is processed on average within of week of receiving the shipment from the waste generator.

A full service laboratory, located on site, is devoted to testing all incoming waste. However, the lab is not set up to process or analyze any environmental testing samples. All environmental testing media is sent to another laboratory for testing. The facility uses passive badge testing to measure atmospheric benzene concentrations. These values are used to determine what form of respiratory protection is needed. On average, it takes 2-3 weeks to receive the results from the badges which is well after the waste has been processed. This report investigated the potential relationship between the benzene values seen in the waste as compared to the values seen from the results of the badge testing. It is hypothesized that a factor based calculation from a comparison of benzene in the waste and atmosphere, similar to what is used in Method 1311: Toxicity Characteristic Leaching Procedure may predict what atmospheric concentrations of benzene would be for certain concentrations seen in waste.

Statistical analysis, including a Pearson correlation, indicated significant variability and a lack of linearity for the waste stream benzene concentration and the atmospheric concentration datasets. Factor calculated atmospheric benzene concentrations displayed a difference of 28% from the observed atmospheric value. This report showed the difficulty in attempting to predict the atmospheric concentration of a chemical for the basis of determining the proper amount of respiratory protection.

Keywords: Benzene, Badge Testing, Prediction

Dedication

I would like to thank my beautiful wife for all her love, patience, and support as I continue to get “my final degree”. I would like to thank my son for all the love and joy you bring in my life.

Acknowledgements

I would like to thank Green America Recycling and Continental Cement for their financial and emotional support. I would like to thank all of my professors at Montana Tech especially Dr. Terry Spear, Dr. Julie Hart, Theresa Stack, and Andy O'Brien for always taking time to help.

Table of contents

ABSTRACT	1
KEYWORDS: BENZENE, BADGE TESTING, PREDICTION	2
DEDICATION	3
ACKNOWLEDGEMENTS	4
LIST OF TABLES	7
LIST OF FIGURES.....	8
LIST OF EQUATIONS	9
 1. INTRODUCTION	 10
1.1. General Information about Benzene	10
1.2. Benzene: Routes of Exposure	12
1.3. Health Effects	12
1.4. Report Objectives	13
2. SITE AND PROCESS DESCRIPTION.....	14
2.1. Site Description	14
2.2. Process Description	16
3. METHODS AND MEASUREMENT	18
3.1. Waste Stream Sample Analysis	18
3.2. Organic Badge Analysis.....	18
4. RESULTS AND DISCUSSION	19
4.1. Amount of Benzene in Waste	19
4.2. Airborne Benzene Concentrations.....	22
4.3. Benzene Factor.....	24
4.4. Comparison of Actual vs. Calculated.....	25

5. CONCLUSION	29
WORKS CITED	32
APPENDIX A: BENZENE CONCENTRATION IN WASTE	33

List of Tables

Table 1: Atmospheric Benzene Concentration	22
Table 2: Benzene Factor Breakdown	25
Table 3: Calculated Atmospheric Benzene.....	26
Table 4: Relative Percent Difference for Mean and Median	26

List of Figures

Figure 1: Benzene Ring	10
Figure 2: Laboratory	15
Figure 3: Process Equipment	16
Figure 4: GC- MS for Organic Analysis.....	17
Figure 5: Normality Test of Waste Stream Benzene	20
Figure 6: Normality Test after Log-Normal Analysis	20
Figure 7: Histogram of the Benzene Found in Waste.....	21
Figure 8: 95% Confidence Intervals for Benzene Concentration in Waste	22
Figure 9: Histogram of OV Badge Results (ppm)	23
Figure 10: Confidence Interval Comparison for Atmospheric Benzene	23
Figure 11: Grouped Comparison of Actual vs. Calculated Benzene Values	27
Figure 12: P Value Comparison of Paired T-test.....	28

List of Equations

Equation 1: Time Weighted Average	10
Equation 2: Standard Error of the Mean	12
Equation 3: Percent Difference	17
Equation 4: Paired T-test Calculation	18

Introduction

1.1. General Information about Benzene

This report is intended to analyze whether there is a potential relationship between the airborne benzene concentration and waste stream source benzene concentration. Benzene is a commonly used flammable liquid whose vapors are found low to the ground due to its higher vapor density (Centers for Disease Control, 2013). It is a sweet smelling aromatic hydrocarbon, seen in Figure 1, which is used in numerous reactions. The atmospheric behavior of benzene indicates it is quite stable, and when compared to other hydrocarbon molecules it is barely photochemically reactive. Reactions that take place with atmospheric benzene result in the formation of phenols, peroxides, epoxides, and aldehydes (Environmental Protection Agency, 1998). The following are 8-hr TWA limits/recommendations: Occupational Safety and Health Administration (OSHA) Permissible Exposure Level (PEL) 1 ppm, National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) 0.1 ppm, and American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) 0.5 ppm (OSHA, 2012).

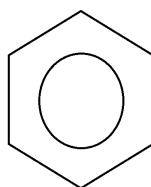


Figure 1: Benzene Ring

Approximately 4 g/l of benzene is found in crude oil (World Health Organization, 2010). Benzene was discovered in the 18th century; however it was not consumed in mass quantities until the 1940's (Environmental Protection Agency, 1998). The petroleum industry is responsible for the majority of benzene produced worldwide (World Health Organization, 2010).

Catalytic refining is responsible for 45% of all benzene produced. Crude oil undergoes catalytic reactions to separate out hydrogen and other carbon containing molecules including aromatic hydrocarbons. The production of ethylene results in about 22% of all benzene produced. Toluene cracking produces around 25% of benzene that is used. Other processes that result in benzene like cracking or recycling from petroleum based materials (Environmental Protection Agency, 1998). Cigarette smoking, volcanoes, food, water, and forest fires are other sources of benzene (Centers for Disease Control, 2013) (World Health Organization, 2010).

Benzene is used commercially at a concentration range of 50%-100% as intermediate for the chemical manufacture of cumene, ethylbenzene, styrene, and cyclohexane (Environmental Protection Agency, 1998). It is used in the manufacture of lubricants, dyes, drugs, glues, and nylon. Benzene is consistently rated as one of the top 20 chemicals used in the United States (Centers for Disease Control, 2013). Benzene is one of the constituents found in gasoline, and is a common way for people to be exposed to benzene.

Gas stations and automotive exhaust are common sources for atmospheric benzene exposure for the general public. Elevated levels of benzene may be found in homes as a result of paint, glues, consumer products, and cigarette smoking (World Health Organization, 2010). People that work in the petroleum or chemical industries are susceptible to higher benzene exposures than most others. Hazardous waste facility workers are also susceptible to elevated values of benzene exposure (Centers for Disease Control, 2013). At the site selected for this study, a substantial portion of the waste received comes from the industries and products listed in the previous paragraph.

1.2. Benzene: Routes of Exposure

The exposure routes for benzene are: dermal, inhalation, ingestion, and skin/eye contact (Centers for Disease Control, 2013). In the occupational environment, ingestion of benzene is usually the result of poor hygiene practices. Inhalation and dermal exposures are the most commonly seen in industry (Arnold, et al., 2013). The use of engineering controls and personal protective equipment helps to reduce benzene exposures. Benzene inhalation is the primary exposure route (Arnold, et al., 2013). Due to the volatility of benzene, benzene is routinely found in the atmosphere when handling anything that contains benzene.

1.3. Health Effects

1.3.1. Acute Exposure

The inhalation of benzene produces different symptoms and illnesses. Alcohol use amplifies the acute effects of benzene exposure. Acute benzene exposure may result in the following symptoms: dizziness, headache, confusion, and drowsiness (World Health Organization, 2010). When benzene concentrations are over 3,000 ppm, anesthetic properties may occur (Klaassen, 2013). If acute benzene poisoning occurs, it can result in an inflamed respiratory tract, renal congestion, and potential pulmonary hemorrhages of a worker (Office of Environmental Health Hazard Assessment, 1999).

1.3.2. Chronic Exposure

Benzene is classified by the International Agency for Research on Cancer (IARC) as Group1 carcinogen (World Health Organization, 2010). Chronic benzene exposure is well-documented that it causes various cancers including Acute Myeloid Leukemia (Arnold, et al., 2013). Elevated levels of benzene poisoning have shown to increase the likelihood of leukemia

formation in exposed individuals. It is proposed that benzene may be responsible for the formation of other forms of leukemia and lymphomas (World Health Organization, 2010).

Research supports that chronic exposure to benzene leads to the reduction of leukocytes, erythrocytes, and platelets, and may lead to the development of aplastic anemia (Arnold, et al., 2013). Ovary size reduction and menstrual cycle changes have been observed in women after the inhalation of large amounts of benzene over a few months (Centers for Disease Control, 2013). Exposure to benzene should be reduced or eliminated as its acute and chronic effects are well documented.

1.4. Report Objectives

The study will obtain and analyze individual datasets for waste stream benzene concentrations and airborne benzene concentrations using descriptive and statistical analysis. The use of a factor based on the waste stream benzene concentration and airborne benzene concentrations will be able to predict airborne benzene concentrations that would determine the appropriate level of respiratory protection. There is a correlation observed between the waste benzene concentrations and airborne benzene concentrations at the waste facility.

2. Site and Process Description

2.1. Site Description

An onsite Portland cement plant is located just south of Hannibal, Mo alongside the Mississippi River. The size of the site is approximately 3500 acres, which includes a mining operation. The cement plant operates a dry process rotary cement kiln to produce Portland cement. A proprietary blend of ground clinker and other materials make up the cement that is sold.

The current process is very energy intensive and requires a significant amount of fuel. This fuel may be composed of natural gas, coal, solid waste derived fuel, and liquid waste derived fuel. The energy recovery of alternative fuels such as solid and liquid waste derived fuels allows for environmental stewardship of hazardous waste by utilizing a process that results with higher destruction removal efficiency.

Green America Recycling (GAR) is located on the same site as a Portland cement plant in Hannibal, Mo. Green America Recycling is a hazardous waste Treatment, Storage, and Disposal Facility (TSDF). The existing capacity allows for the storage of large quantities of solid and liquid waste derived fuel. There are certain restrictions on what fuels can be accepted and processed. Waste comes from all across North America, mainly the United States. The fuel is delivered to the cement plant as fuel. This process is an environmentally conscious alternative for the disposal of hazardous waste.

Workers are exposed to different chemicals on a day-to-day basis, and protective measures are in place reducing or eliminate any potential exposure. Administrative controls rotate employees around to different jobs and areas to reduce exposure. Control rooms, enclosed cabin mobile equipment, and ventilation are engineering controls to reduce or eliminate chemical

exposure at or above the PEL. The use of personal protective equipment is intended to reduce or eliminate chemical exposure.

An on-site laboratory has the ability to test waste streams for energy value, halogen composition, total metals, polychlorinated biphenyls analysis, mercury, pH, water content, and organic composition. The laboratory has instrumentation that is valued well over one million dollars as seen in Figure 2. The laboratory has the following instruments for use: bomb calorimeters, ion chromatograph systems, inductively coupled plasma-optical emission spectrometers, mercury cold vapor atomic absorption spectrometer, gas chromatograph (GC), and gas chromatograph coupled with mass spectrometers (GC-MSD). The laboratory follows a Quality Assurance/Quality Control program, and participates in a nationwide testing program with other laboratories. The 2015 nationwide blind testing program indicated that the laboratory had an acceptance rate >95% for the testing the lab participated in.



Figure 2: Laboratory

Wastes have the ability to come in all forms and sizes. Solid waste may come in bulk trucks, boxes, or by drums. Drums and bulk trucks are processed to ensure the waste goes into

the solid waste fuel. There is plenty of storage available for solid fuel. This allows GAR to blend solid waste to the specifications that were given by the cement plant.

Liquid waste may come in by bulk or drums. Bulk liquid waste is pumped directly into the tank storage farm. Liquid drums are fed through a “unique” mixing station that enables it to be transferred into our tank farm. The material is able to be blended with liquid fuel in our “unique” mixing station, and pumped over to our tanks. Fuel is blended to specifications before being supplied to the cement plant for usage.

2.2. Process Description

Different processes are performed on-site to prepare waste for thermal recovery. The process of interest is a multi-step process that allows for sludge like material to be combined with various liquids, so that the sludge is now in the liquid as illustrated in Figure 3. Due to the handling difficulty of sludge, sludge must be blended with liquid fuel. Sludge may increase or decrease energy value, halogen concentration, and metals concentration. Depending upon what liquids and sludge are currently in storage, a “recipe” can be made. This report will examine a particular waste for comparative purposes.



Figure 3: Process Equipment

The initial step of the process is obtaining a sample for testing in the Fuels Laboratory. An individual obtains a sample after the waste has been put in the solidification pit. This task is performed on supplied air due to the potential of benzene exposure of this waste stream. The sample is brought to the laboratory to determine energy content, halogen, and metal analysis. In addition to the previous analysis, a sample is prepared for analysis by Gas Chromatograph-Mass Spectrometer (GC-MS) as seen in Figure 4. The GC-MS analysis is able to determine the amount of benzene in the waste.



Figure 4: GC- MS for Organic Analysis

The laboratory approves the shipment for processing. Processing consists of emptying the shipment container into a segregated area known as the solidification unit. It located inside another building, and allows for the processing of sludge waste. The shipment is emptied into this area by gravitational forces. Once in the area, a plastic liner must be removed before the sample is processed. The plastic liner is processed with other solid material that is received.

Employees feed the sludge with a skid loader. The skid loader is connected with a devoted supplied airline that the operator can connect to. Due to the uncertainty of atmospheric concentration, this operator is required to use supplied air and not rely solely on organic-vapor cartridges. The operator oversees the auguring of material into the liquid fuel tank farm. Once in the tank farm, exposures to the waste's emissions are eliminated. On average, this person would do this for a maximum of 8 hours a day.

3. Methods and Measurement

3.1. Waste Stream Sample Analysis

A composite grab sample of the waste was taken by the GAR Operations Department, and was sent to the lab for analysis. The grab sample was then extracted by acetone. The extracted sample was analyzed via GC-MS. A quantification of benzene is performed based on the annual calibration of the instrument. A total of a 189 waste stream samples were analyzed.

3.2. Organic Badge Analysis

The operator of the skid loader had a 3m Organic Vapor Passive Badge placed on him during operation. The badge was clipped to the outside of his chemical resistant coverall around their breathing zone. No area atmospheric testing was performed, as this area is only used when processing material like this. The badge was collected and shipped to ALS Laboratory, an AIHA accredited laboratory, for analysis using the 3M Organic Vapor Monitor Sampling and Analysis Guide. The average sampling duration was 8 hours and the results were reported in ppm. For all samples that were not an 8-hour TWA, samples were converted to an 8-hour TWA using equation 1. A total of 13 samples were taken. The following equation was used (Occupational Safety and Health Administration, 2006).

$$TWA = (C_1 T_1) / T_x \quad (1)$$

where C is observed concentration, T_1 is time of exposure(minutes), T_x is shift duration(minutes)

4. Results and Discussion

4.1. Amount of Benzene in Waste

Benzene values were calculated using a GC-MS. It proved to be easy and cost effective for our laboratory to analyze these samples in-house. There was no additional training or instrumentation needed to complete the analysis. The results were reported in ppm. The waste benzene values will play an important role in the development of a standardize factor to predict atmospheric benzene concentrations based on the concentration from the waste and observed atmospheric concentrations.

The sample was extracted with acetone, which is commonly used in the in-house preparation of solid samples for analysis on the GC-MS. All but one of the samples analyzed had a significant amount of benzene. One of the samples was below the practical quantitation limit, and was reported to be less than 10 ppm. There were a total of 189 samples analyzed. Waste stream benzene concentrations are reported in Appendix A: Benzene Concentrations in Waste. The range of the raw benzene concentration in waste is from <10 ppm to 29,643 ppm. The mean was 5126 ppm. The standard deviation is 5518. It appears that the standard deviation is greater than the calculated mean, which shows that there is tremendous variability in the raw data.

To determine if the raw data had normal distribution, a normality test displayed in Figure 5 was performed. It was determined that data natural log should be tested to determine normal distribution. The normal distribution of that data, shown in Figure 6, indicates that it behaves in a normal fashion.

The data appears to have normal distribution after performing a log-normal analysis. A histogram of the normalized data is shown in Figure 7 shows the overall distribution.

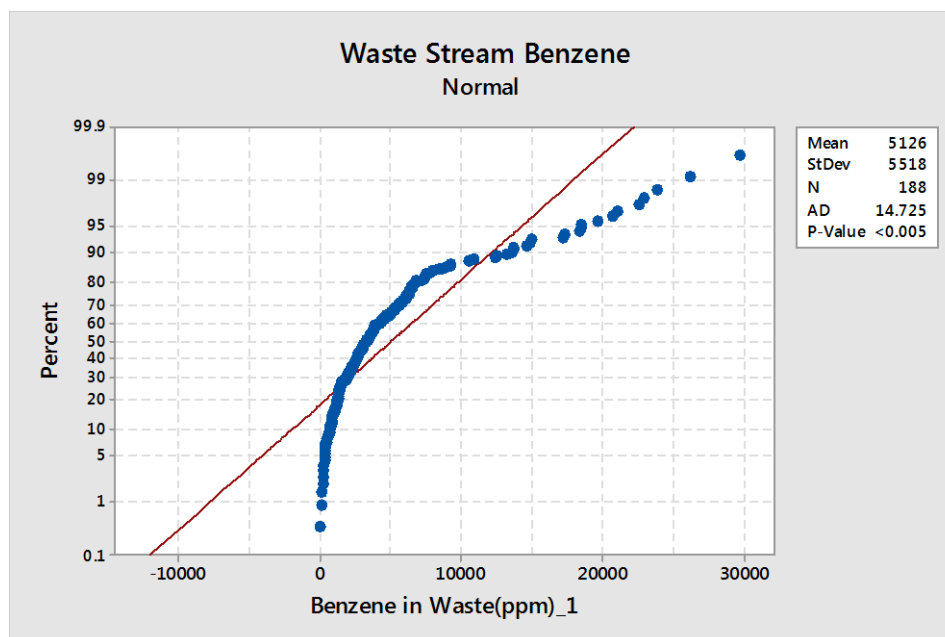


Figure 5: Normality Test of Waste Stream Benzene

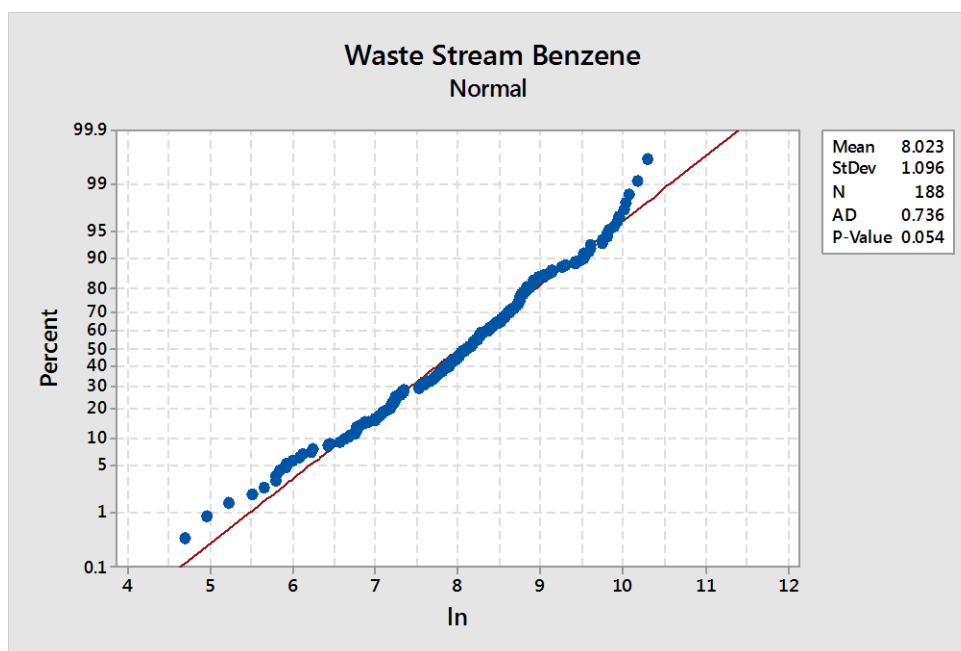


Figure 6: Normality Test after Log-Normal Analysis

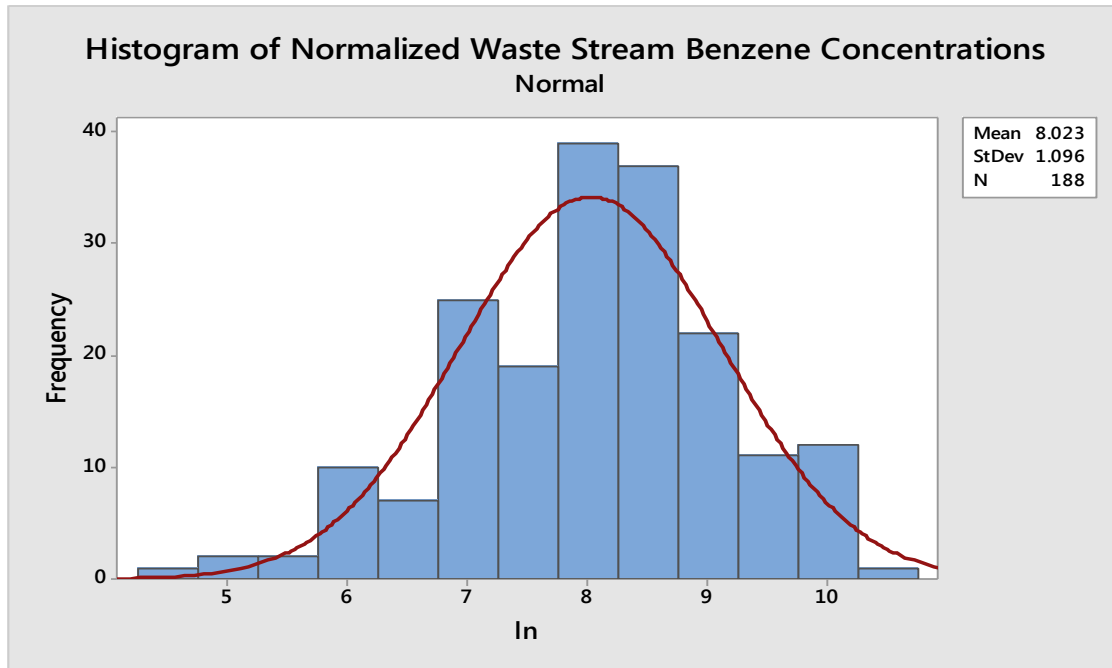


Figure 7: Histogram of the Benzene Found in Waste

The standard error of the mean (SE) allows for the creation of confidence intervals if there would be another round of samples taken for that same sample set (Minitab, 2015). This takes into account any difference or variability that may be seen within multiple samples. It is obtained by the following Equation 2:

$$SE = \sigma / \sqrt{n} \quad (2)$$

Where σ is Standard Deviation, n is number of samples taken

Using the standard error of the mean, a 95% confidence interval was able to be established. That interval was produced graphically with Minitab along with the median

confidence interval in Figure 8: 95% confidence interval of the mean. The results indicate that there is overlapping of the confidence intervals of the median and mean.

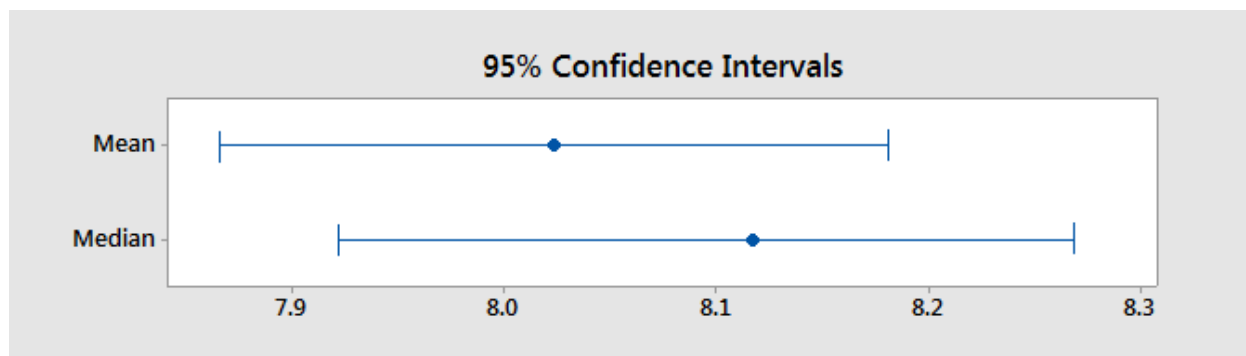


Figure 8: 95% Confidence Intervals for Benzene Concentration in Waste

4.2. Airborne Benzene Concentrations

Organic Vapor badges were sent to be analyzed by ALS Laboratories. Airborne concentrations reported in Table 1 are reported in an 8-hour TWA.

Table 1: Atmospheric Benzene Concentration

Sample #	Date	OV Badge(ppm)
1	11/3/2014	3
2	11/3/2014	5.1
3	11/5/2014	4.9
4	10/13/2014	2.3
5	10/14/2014	5
6	8/5/2014	2
7	8/7/2014	0.9
8	8/8/2014	7.5
9	8/8/2014	4
11	9/8/2014	1.7
12	9/11/2014	2.1
13	9/9/2014	2.1

The minimum and maximum of the atmospheric samples was from 0.9 ppm to 7.5 ppm for a range value of 6.6 ppm. A histogram is also provided in Figure 8. The mean benzene concentration was 3.38 ppm.

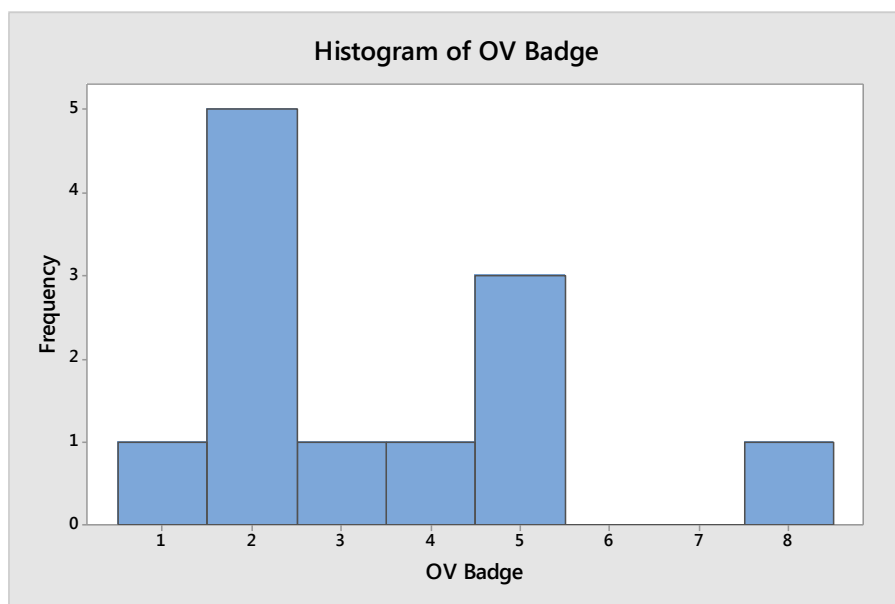


Figure 9: Histogram of OV Badge Results (ppm)

The standard deviation and SE was calculated using Minitab, and the standard deviation of 1.9239, while the SE was 0.555. The 95% confidence intervals for the mean and median are respectively, 2.16 ppm to 4.6ppm and 2.0263ppm to 4.9737ppm. Unlike the benzene in the waste, the median and mean confidence intervals are quite similar, with the mean interval being completely contained inside the median interval. A graphical interpretation of is seen in Figure 9.

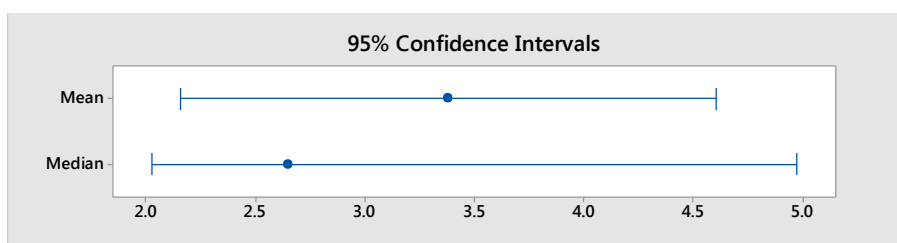


Figure 10: Confidence Interval Comparison for Atmospheric Benzene

4.3. Benzene Factor

The idea of developing a factor to be used for respirator guidance comes from my experience in a laboratory and my knowledge of EPA test methods. The Toxicity Characteristic Leaching Procedure (TCLP) is EPA test method 1311, used to determine toxicity of waste, or whether or not a waste is considered hazardous due to its toxicity. In Method 1311, a generator may analyze a solid for total constituent analysis in lieu of TCLP procedure. The total constituents may be divided by a factor of 20 to determine if it displays any toxicity (US EPA, 2012) The hypothesis of this report is derived from this concept.

To develop the factor, atmospheric benzene concentrations and waste stream concentrations were arranged for comparative purposes to see when both analysis were performed. Atmospheric and waste stream testing occurred 13 times on the same day. There were some instances in which waste stream sampling was able to happen more than once a day due to the volume of waste being processed. In these instances, an average of the waste stream concentration was taken. To determine whether there is a correlation between waste stream benzene concentration and airborne benzene concentration, a Pearson correlation test was performed. The P-value, 0.176, from the Pearson correlation indicates that there is not a significant relationship between the two datasets.

To develop a factor, it was decided to use the organic vapor badge data as the denominator and using the waste amount as the numerator. This was done for every pair of data as seen in Table 2 below. A final factor of 2.73 was calculated by taking an average of all the individual factors. The final factor will be used to predict the calculated atmospheric benzene concentrations based on the amount that was seen in the waste samples.

Table 2: Benzene Factor Breakdown

Date(m-d-y)	Waste	OV	Factor
11/3/2014	7.059618	3	2.353206
11/3/2014	8.006368	5.1	1.569876
11/5/2014	7.824046	4.9	1.596744
10/13/2014	7.975908	2.3	3.467786
10/14/2014	6.927558	5	1.385512
8/5/2014	7.724888	2	3.862444
8/7/2014	5.805135	0.9	6.45015
8/8/2014	7.185387	7.5	0.958052
8/8/2014	6.880384	4	1.720096
9/8/2014	6.821107	1.7	4.012416
9/11/2014	4.969813	2.1	2.366578
9/9/2014	6.448889	2.1	3.0709
		Mean	2.73448

4.4. Comparison of Actual vs. Calculated

Calculated values were determined by dividing the amount of benzene found in the waste divided by the factor that was identified above. These results may be seen in table 3. As a result, calculated atmospheric benzene values were obtained. A comparison of the mean between the actual and calculated was performed. A relative percent difference, Equation 3, calculation was performed using the following formula under the assumption that these are both atmospheric concentrations.

$PD(\%) = ((\text{Abs}(\text{Actual} - \text{calculated})) / ((\text{Actual} + \text{Calculated}) / 2)) * 100 \quad (3)$
where Abs is absolute value, actual is actual value, calculated is calculated value

Table 3: Calculated Atmospheric Benzene

Date(m-d-y)	Waste	OV	Factor	Predicted
11/3/2014	7.059618	3	2.353206	2.581704
11/3/2014	8.006368	5.1	1.569876	2.927931
11/5/2014	7.824046	4.9	1.596744	2.861256
10/13/2014	7.975908	2.3	3.467786	2.916792
10/14/2014	6.927558	5	1.385512	2.53341
8/5/2014	7.724888	2	3.862444	2.824994
8/7/2014	5.805135	0.9	6.45015	2.122939
8/8/2014	7.185387	7.5	0.958052	2.627698
8/8/2014	6.880384	4	1.720096	2.516158
9/8/2014	6.821107	1.7	4.012416	2.494481
9/11/2014	4.969813	2.1	2.366578	1.817462
9/9/2014	6.448889	2.1	3.0709	2.35836
	mean	3.383333		2.548599
	Median	2.65		2.557557

Table 4: Relative Percent Difference for Mean and Median

	Actual	Calculated	Difference	Percent Difference
Mean	3.38	2.55	0.91	28%

The percent difference for the mean is 28%. It was my hope that these values would be less than 20% -15%. This comes from my experience in a laboratory where these values are standards used in Quality Assurance testing.

For a comparison of the means, a paired t-test is required. A paired t-test was ran on the following assumption and hypothesis:

Assumption: The calculated value is dependent upon the OV badge value and thus a paired test is needed.

Null Hypothesis: There is no difference between the mean differences.

Alternative Hypothesis: There are significant differences between the means

A one tailed t test is being used instead of a two-tailed. The concern is on the larger atmospheric concentrations and not on the lower side. Mandatory respiratory protection allows for protection up to 5 ppm using the ACGIH Threshold Limit Values. While using the OSHA PEL would allow for a large MUC, it was decided that the more conservative ACGIH value would be used. A comparative graph was composed to see if there were any trends that could be seen to the eye. The actual and calculated value were graphed against each other to see if there were any major differences that could be identified as suspected outliers or questionable data points. The graph seen below in Figure 11, and indicates that there are no unusual differences in the paired data.

It appears that the calculated values are usually lower than the actual concentrations as seen in Figure 11. The results indicate that maybe the calculated factor is too large, and as a result may underreport the atmospheric conditions if used.

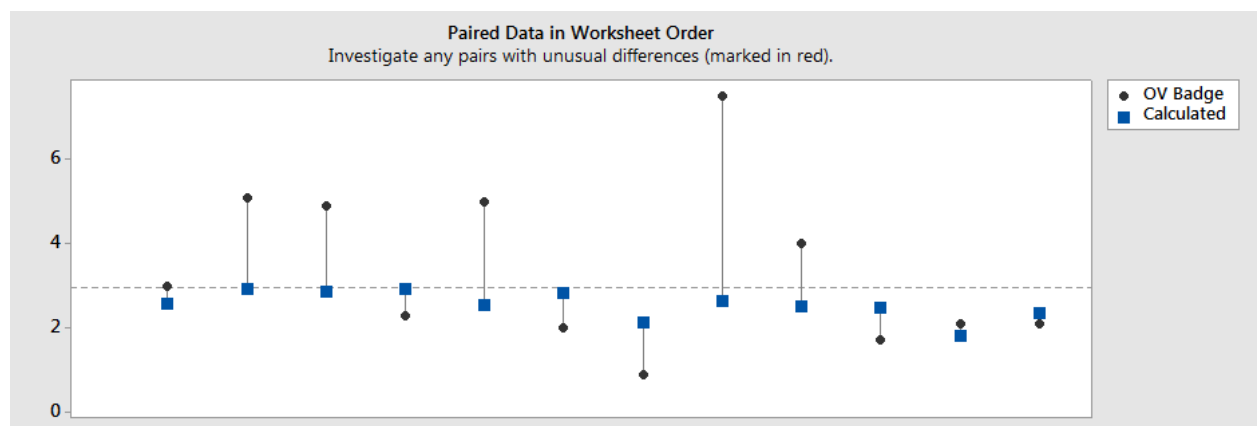


Figure 11: Grouped Comparison of Actual vs. Calculated Benzene Values

A t test was performed using Minitab 17 software. A paired t-test is calculated using the following formula in

4(Janicak, 2007):

$t = (D - 0) / (SD / \sqrt{n}) \quad (4)$
where D is mean difference, SD is standard deviation, and n is the number of paired observations

A paired t-test is used under the assumption that the calculated atmospheric concentration is an observation along with the actual values from the organic badge testing. The calculated t-value, using Minitab 17, is 1.6. The given t value for a 95% confidence is 1.78 for a single side of the curve. Data indicates that the mean would fall under the unshaded portion of the curve or the majority of the curve, and the null hypothesis is proven correct.

The t-test showed that the two mean values were statistically the same with a P value of 0.138. A graphical interpretation, Figure 12, of P indicates that it falls well to the right of the statistically different mean values. It should be noted that the number of samples used was 13, and the more amount of samples would help to validate that the mean values are similar.

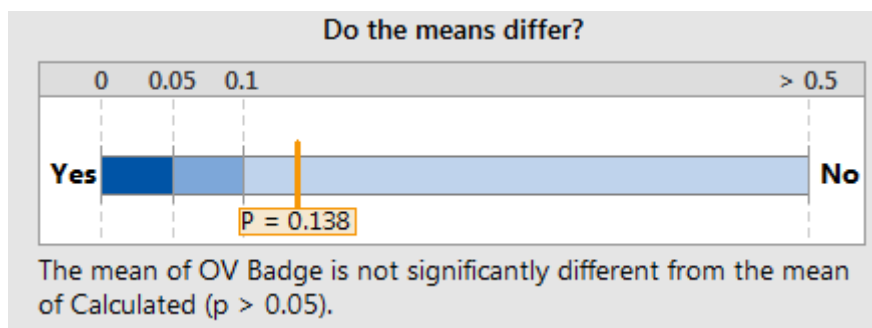


Figure 12: P Value Comparison of Paired T-test

5. Conclusion

This report examined the correlation of waste stream benzene concentrations and airborne benzene concentrations, and whether a factor could be derived from them. If confirmed, individuals would be able to make an informed confident decision on what form of respiratory protection would be needed. Whether it is a full-face respirator or a supplied air respirator, adequate respiratory protection would be in place.

The benzene concentration was quantified for 189 waste samples. The large amount of samples should provide a normal trend of behavior. Instead, a range of almost 30,000 ppm was seen. The standard deviation was greater than the mean, which proves that there is a significant amount of variability. The data, after undergoing a log-normal analysis, appears to have normal distribution. The waste stream benzene concentrations could have been influenced or limited by work practices like waste stream sampling.

The results from the organic vapor badge testing indicated that the mean and median confidence intervals were quite similar with the mean being contained within the range of the median. However, the major limitation to these results is the relatively small sample size. There is some uncertainty with a dataset this small, so additional sampling would be recommended to reduce uncertainty and try to normalize the dataset.

The benzene factor is a calculation based on the benzene values seen in waste divided by values seen in badge testing. A Pearson correlation was performed to indicate how strong of a relationship there was between the waste stream benzene concentrations and airborne benzene concentrations. The p value from the Pearson correlation indicated that the waste stream benzene concentrations and atmospheric benzene concentrations do not have a significant relationship.

The benzene factor would benefit from additional samples of the waste stream and air at the same time. This may prove to be difficult due to the excess time and expense needed for sampling. After all, supplied air is readily available with a devoted source on-site that is already paid for. The supplied air would result in a higher APF to offset any risk with the using a factor-based calculation.

A calculated dataset was generated using the waste results divided by the benzene factor. Basic statistics showed that the difference of the mean 28% difference in values between the observed and calculated benzene values. In my experience in a lab, this value should be well below 20%. A graphical comparison showed that a majority of the badge samples were higher in concentration, but there were some instances in which the roles switched. I would have thought that there would be an identifiable trend. To see how similar the calculated and observed values were, a paired t-test was performed to test the mean values. Surprisingly, the p value from the t-test indicates that the means are not statistically different.

This study has its limitations. The 189 waste stream benzene results show great variability and its population size is over ten times the population size of the badge testing. It should be noted that there needs to be additional corresponding waste and air testing so that there datasets are equal in size. This may be costly for the facility and time consuming, but will produce better statistical analysis. The time for airborne benzene sampling was limited based on the amount of waste available for processing. If a consistent amount of waste was available for processing, it would help to keep the sampling time approximately the same. The data has limitations. The waste stream samples had to undergo a log-normal analysis to display a normal distribution. The atmospheric samples were limited to the small sample size, but displayed a normal distribution

The facility's ventilation rates may have been limited based upon how well the cement kiln was running. If the cement kiln is shutdown, all ventilation is pulled through carbon canisters instead of being exhausted into kiln. The ventilation rate may have been impacted if the carbon canisters were past their service life.

Airborne samples taken during August and September were exposed to elevated temperatures and humidity. During these months, employees will use additional fans and open up doorways to increase air flow to reduce their body temperature. Employees, in the months of October and November, will reduce exposure to the colder outside temperature by closing the building. The varying temperatures may alter the emittance of benzene from the waste stream. The stated limitations and statistical results to this factor based approach prove that there is too much uncertainty involved in using this.

Works Cited

- Arnold, S. M., Angerer, J., Boogaard, P., Hughes, M. F., O'Lone, R. B., Robinson, S. H., & Schnatter, A. R. (2013). The use of biomonitoring data in exposure and human health risk assessment: benzene case study. *Critical Reviews in Toxicology*, 119-153.
- Centers for Disease Control. (2013, February 14). *Facts About Benzene*. Retrieved from Centers for Disease Control: <http://www.bt.cdc.gov/agent/benzene/basics/facts.asp>
- Environmental Protection Agency. (1998). *Locating and Estimating Air Emissions From Sources of Benzene*. Research Triangle Park: USEPA Office of Air Quality.
- Klaassen, C. D. (2013). *Casarett & Doull's Toxicology: The Basic Science of Poisons*. New York: McGraw Hill Education.
- Minitab. (2015). *minitab 17 Support*. Retrieved from Minitab: <http://support.minitab.com/en-us/minitab/17/topic-library/basic-statistics-and-graphs/hypothesis-tests/tests-of-means/what-is-the-standard-error-of-the-mean/>
- Office of Environmental Health Hazard Assessment. (1999). *Acute Toxicity Summary: Benzene*. California OEHHA.
- OSHA. (2012, 9 6). *Chemical Sampling Information Benzene*. Retrieved from United States Department of Labor: Occupational Safety and Health Administration: https://www.osha.gov/dts/chemicalsampling/data/CH_220100.html
- United States Department of the Navy. (2013). *Respirator Fit Testing*. Washington DC: United States Department of Defense.
- World Health Organization. (2010). *Exposure to Benzene: A major public health concern*. Geneva: WHO.

Appendix A: Benzene Concentration in Waste

Date	SID	Benzene in PPM	Norm. Benzene
9/23/2014	1	1164	7.05961763
9/23/2014	2	3000	8.00636757
9/23/2014	3	2500	7.82404601
9/23/2014	4	2910	7.97590836
9/23/2014	5	1020	6.92755791
9/23/2014	6	2264	7.72488844
9/23/2014	7	332	5.80513497
9/23/2014	8	1320	7.18538702
9/23/2014	9	973	6.88038408
9/23/2014	10	917	6.82110747
9/23/2014	11	144	4.9698133
9/23/2014	12	632	6.44888939
9/23/2014	13	1262	7.14045304
9/23/2014	14	329	5.79605775
9/23/2014	15	517	6.24804287
9/23/2014	16	1390	7.23705903
9/23/2014	17	1210	7.09837564
9/23/2014	18	1370	7.22256602
9/23/2014	19	3810	8.24538447
9/23/2014	20	1870	7.53369371
9/23/2014	21	1107	7.00940893
9/23/2014	22	505	6.22455843
9/23/2014	23	1541	7.34018684
9/23/2014	24	1515	7.32317072
9/23/2014	25	878	6.77764659
9/23/2014	26	1092	6.99576616
9/23/2014	27	441	6.08904488
9/23/2014	28	377	5.93224519
9/23/2014	29	1318	7.18387072
9/23/2014	30	2371	7.77106709
9/24/2014	31	1871	7.53422833
9/24/2014	32	1401	7.24494155
9/24/2014	33	1363	7.21744343
9/24/2014	34	2286	7.73455884

9/24/2014	35	2722	7.90912218
9/24/2014	36	1457	7.28413481
9/25/2014	37	943	6.84906628
9/26/2014	38	4008	8.29604764
9/26/2014	39	3033	8.01730751
9/26/2014	40	7930	8.97840831
9/29/2014	41	1497	7.31121838
9/29/2014	42	615	6.42162227
9/30/2014	43	1543	7.34148385
9/30/2014	44	1359	7.21450441
9/30/2014	45	1962	7.58171964
10/1/2014	46	1989	7.59538728
10/1/2014	47	2183	7.68845536
10/1/2014	48	1341	7.20117088
10/2/2014	49	375	5.92692603
10/7/2014	50	1134	7.03350648
10/7/2014	51	853	6.74875955
10/7/2014	52	4926	8.50228258
10/7/2014	53	5260	8.56788631
10/7/2014	54	3684	8.2117544
10/8/2014	55	3684	8.2117544
10/8/2014	56	7502	8.92292493
10/8/2014	57	<10	#VALUE!
8/9/2014	58	1200	7.09007684
8/9/2014	59	877	6.77650699
8/9/2014	60	2018	7.6098622
10/10/2014	61	2789	7.93343839
10/13/2014	62	246	5.50533154
10/13/2014	63	345	5.84354442
10/13/2014	64	287	5.659482216
10/15/2014	65	2322	7.750184162
10/15/2014	66	6320	8.751474487
10/15/2014	67	6460	8.773384597
10/16/2014	68	10900	9.296518068
10/16/2014	69	7990	8.985946039
10/17/2014	70	3475	8.153349758
10/17/2014	71	6497	8.779095811
10/28/2014	72	458	6.126869184

10/28/2014	73	404	6.001414878
10/28/2014	74	754	6.625392368
10/28/2014	75	185	5.220355825
10/28/2014	76	110	4.700480366
10/28/2014	77	1405	7.247792582
10/28/2014	78	788	6.66949809
10/31/2014	79	4424	8.394799543
10/31/2014	80	2457	7.806696373
10/31/2014	81	2719	7.908019445
10/31/2014	82	2582	7.856319571
10/31/2014	83	3030	8.016317899
10/31/2014	84	2304	7.742402022
10/31/2014	85	3956	8.282988693
10/31/2014	86	868	6.766191715
10/31/2014	87	809	6.695798917
10/31/2014	88	2756	7.921535632
10/31/2014	89	2954	7.990915463
10/31/2014	90	8537	9.052164937
11/3/2014	91	6386	8.761863373
11/3/2014	92	1866	7.531552381
11/3/2014	93	1257	7.136483209
11/4/2014	94	1535	7.33628566
11/4/2014	95	3495	8.159088655
11/5/2014	96	2340	7.757906208
11/6/2014	97	2484	7.817625443
11/7/2014	98	5266	8.56902634
11/7/2014	99	3602	8.189244526
11/10/2014	100	3960	8.283999304
11/10/2014	101	6265	8.742733867
11/10/2014	102	2669	7.889459149
11/11/2014	103	3899	8.268475389
11/11/2014	104	6820	8.827614751
11/11/2014	105	6555	8.787983396
11/11/2014	106	7397	8.908829792
11/12/2014	107	7506	8.92345798
11/13/2014	108	8871	9.090542809
11/14/2014	109	13725	9.526974266
11/14/2014	110	29653	10.29731858

11/17/2014	111	9319	9.139810606
11/17/2014	112	6748	8.817001444
11/18/2014	113	12481	9.431962767
11/19/2014	114	5141	8.545002892
11/21/2014	115	10557	9.264544426
12/9/2014	116	5895	8.681859813
12/9/2014	117	4562	8.425516403
12/9/2014	118	5942	8.689801056
12/9/2014	119	4739	8.463581422
12/9/2014	120	13231	9.49031784
12/9/2014	121	715	6.572282543
12/9/2014	122	2128	7.66293785
12/9/2014	123	2591	7.859799181
12/9/2014	124	5756	8.657998068
12/9/2014	125	2070	7.635303886
12/11/2014	126	18327	9.816130661
12/11/2014	127	18461	9.823415678
6/16/2015	128	23894	10.08138266
6/16/2015	129	22927	10.04007053
6/26/2015	130	6150	8.724207361
6/26/2015	131	4970	8.511175119
6/26/2015	132	20660	9.935954743
6/26/2015	133	5380	8.590443653
6/26/2015	134	5280	8.571681377
7/2/2015	135	26163	10.17210148
7/2/2015	136	3922	8.274357007
7/2/2015	137	6301	8.74846363
7/10/2015	138	2176	7.685243608
7/10/2015	139	4249	8.35443894
7/10/2015	140	4437	8.397733751
7/10/2015	141	3371	8.122964715
7/10/2015	142	5514	8.615045592
7/16/2015	143	15047	9.618933915
7/16/2015	144	9318	9.139703292
7/16/2015	145	18446	9.822602824
7/16/2015	146	5632	8.636219898
7/16/2015	147	7372	8.905444319
7/24/2015	148	5070	8.531096097

7/24/2015	149	21050	9.954655839
7/24/2015	150	6150	8.724207361
7/24/2015	151	17304	9.758692968
7/31/2015	152	3070	8.029432841
7/31/2015	153	22530	10.02260303
7/31/2015	154	7210	8.88322423
7/31/2015	155	6560	8.788745882
7/31/2015	156	5080	8.533066541
8/12/2015	157	3730	8.224163513
8/12/2015	158	3840	8.253227646
8/12/2015	159	3010	8.009695358
8/12/2015	160	8480	9.045465729
8/20/2015	161	3330	8.110727583
8/20/2015	162	3590	8.185907481
8/20/2015	163	6110	8.717682052
8/20/2015	164	3900	8.268731832
8/20/2015	165	3550	8.174702882
8/26/2015	166	6390	8.762489547
8/26/2015	167	6810	8.826147399
8/26/2015	168	4300	8.366370302
8/26/2015	169	2700	7.901007052
8/26/2015	170	5650	8.639410824
9/4/2015	171	13600	9.517825072
9/4/2015	172	3280	8.095598701
9/4/2015	173	4360	8.380227336
9/4/2015	174	4700	8.455317788
9/15/2015	175	4530	8.418477218
9/15/2015	176	14690	9.594922269
9/15/2015	177	6090	8.714403361
9/15/2015	178	3100	8.03915739
9/15/2015	179	12500	9.433483923
9/15/2015	180	13710	9.525880773
9/15/2015	181	14830	9.604407435
9/15/2015	182	17180	9.751501196
9/23/2015	183	19670	9.886849911
9/23/2015	184	3250	8.086410275
9/23/2015	185	2750	7.919356191
9/23/2015	186	1400	7.244227516

9/28/2015	187	3170	8.061486867
9/28/2015	188	3390	8.1285852
9/28/2015	189	2470	7.81197343