

**Detection of Trace Volatile Organics in Small Roadway Bodies
of Water in the Lake Macatawa Watershed**

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I) Introduction

With a growing awareness of environmental issues, people are becoming more conscious about and interested in the impact they are leaving on the environment. One area of increased concern is the effect of water containments on an ecosystem.

VOC's (volatile organic compounds) are lightweight organics that can easily escape from the liquid into the gaseous state. A particular subset of VOCs called BTEX (benzene, toluene, ethylbenzene, and xylene) are of interest due to their harmful health and environmental effects as well as presence in many commonly used products. BTEX are found in petroleum derivatives such as gasoline, oil, synthetic rubber or plastic, paint thinners, etc. Common exposures in the environment are leaking storage tanks, spills, and exhaust emissions.

Once dissolved into the water, BTEX can represent a direct threat to ecosystems. Documented human health effects are eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Benzene is also a known human carcinogen. (EPA) Considering these observed symptoms in humans exposed to BTEX, these compounds are also likely detrimental to the health of organisms that live in a watershed. The EPA has a toxicity database for aquatic life. Based on EPA data, goldfish have a 90-hour LC₅₀ of 34,420 ug/L for benzene and 94,440 ug/L for ethylbenzene. (EPA) Having levels of VOCs at or around those would have serious implications on the watershed.

One important pathway BTEX get into the environment is by exhaust from passing traffic. Once expelled in the exhaust, BTEX can cool, fall out of suspension in the air and land in the water. They can also remain volatilized, equilibrate with the water surface and become dissolved. In addition to this, since BTEX are volatile, they have a low boiling point and evaporate easily. Therefore, any leaked oil or fuel will more than likely just volatilize into the air unless washed into the water system relatively quickly after being spilled. Regardless of the pathway, once dissolved in water, BTEX have been documented to have a half-life of up to around a year. (Njobuenwu et al) This means that accumulation can occur over time if water flow into and out of an area is minimal. If enough traffic goes by and a high concentration accumulates this could pose risks for the watershed ecosystem. In addition, while the local communities do not get their drinking water directly from the watershed some of the water could contaminate an aquifer that is used for drinking water and enter humans through ingestion.

The purpose of this study was to try and quantify the amount of BTEX present in bodies of water near roadways to try and correlate between traffic levels and concentration present. By identifying areas of high contamination it is possible to better manage and care for the watershed.

II) Methods

The methods used in this study were based largely off of a study by Almedia and Boas in the *Journal of Environmental Monitoring* article "Analysis of BTEX and other substituted benzenes in water using headspace SPME-GC-FID: Method validation." The one major deviation was that the closest column available to the one outlined in the

procedure was a shorter 15m, DB-1301 (USP layer G43), 0.25 mm ID, 1.0 μm 6% cyanopropyl-phenyl 94% methyl polysiloxane.

Step one was determining where the BTEX compounds came out on the column. This was accomplished by making a 2% solution of each compound in pentane and doing a split injection into the GC. Once determined, a standard of all four compounds was made by first dissolving the components in dichloromethane to make a 100 ppm solution. This solution was then diluted with water to make standards of increasingly small concentrations (from 100ppm to 0.1ppb). These were then tested using the SPME to determine the detection limit of the SPME fibers. Each sample was placed in a 40-mL brown glass vial with a septum cap (Sigma-Aldrich). A 10mL headspace was left. The sample was then placed in a water bath at 50 degrees Celsius for 30 minutes while the SPME was inserted in the vial and the fiber exposed in the headspace. Replicates were done on all of the standards and blanks run before each set of samples. Upon getting consistent results from this the data were used to construct a standard curve for each of the compounds (Figure 1-4).

Step two was to determine if BTEX could move from an exhaust sample into an aqueous solution. This was accomplished by collecting samples of exhaust from both a gasoline (1990 Acura Integra) and diesel (2006 VW Jetta) vehicle. These were then exposed to water and SPME used to extract the organics.

Once BTEX was found to be present and detectable in car exhaust, samples sites were chosen. Four initial sites (3 off 31N and 1 off 16th street) were sampled. All the sampling was done at least 2 days after a major rain event. The samples were preserved with three drops of 6 M HCl and stored on ice to prevent volatilization. The samples were then run with the SPME on the GC-FID. A replicate was done on every 1 in 5 samples run. Upon running these samples the SPME needles were upgraded to Divinylbenzene/Carboxen/Polydimethylsiloxane to try to increase detection sensitivity. Another set of 6 samples were collected and run as well as 6 standards (between 0.1 and 70 ppb) to get a new standards curve for the new needles. In addition to this a blank of water was run to see if any of the peaks showing up in the samples were due to a plasticizer in the cap.

To conclude the study, samples were taken in Lake Macatawa near the marina to try and detect the leaking storage tank. Two samples were also taken at a gas station. One was a puddle that had been sitting for a couple of days. The second was a water sample that had been poured over the asphalt and then recollected to try and simulate runoff in a rain event.

III) Results

A. Retention Times

Based on the samples of pure compound run individually the retention times for the BTEX compounds were determined as recorded in Table 1. The order of elution was Benzene, Toluene, Ethylbenzene and *m*-Xylene.

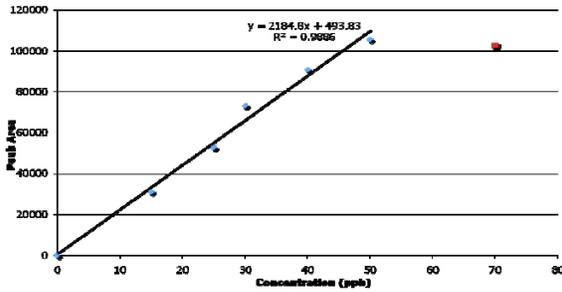
Table 1. BTEX Retention Times

Chemical	Retention Time (min)
Benzene	5.5
Ethylbenzene	13.2
Toluene	9.5
Xylene	13.4

B. Calibration

The peak areas from the standards were used to create a calibration curve for each of the BTEX compounds. Most of the standards run had replicates so the average of the two areas was used when possible. The following four figures (Figures 1-4) are the calibration curves with their respective detection limits.

Figure 1. Benzene Calibration Curve
Detection Limit: 15ppb



*Note that the last point at 70 ppb was not included in the calibration curve since it appeared the needle might have been saturated at this point.

Figure 2. Toluene Calibration Curve
Detection Limit: 3ppb

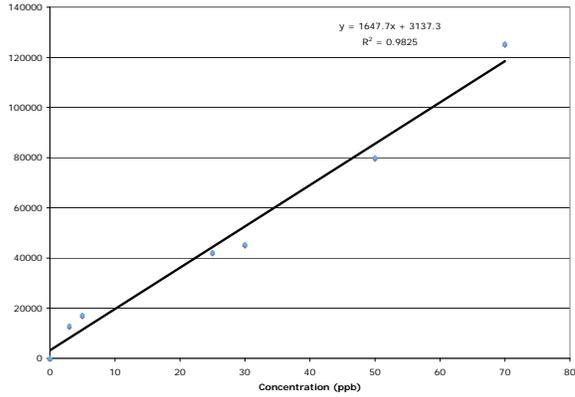


Figure 3. Ethylbenzene Calibration Curve
Detection Limit: 3ppb

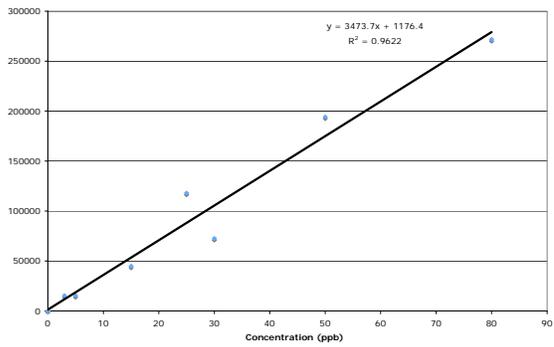
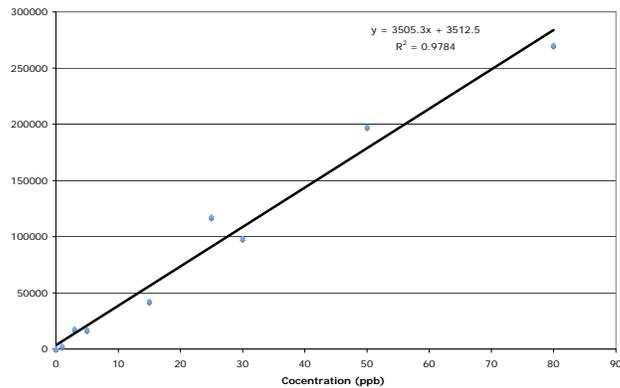


Figure 4. *m*-Xylene Calibration Curve
Detection Limit: 1ppb



C. Quality Control – t-test

To ensure the results obtained were repeatable a student t-test (Case 2) was done. The $T_{\text{calc}}=0.505$ and $t_{\text{table } 95\%}=2.131$. Since $T_{\text{calc}} < t_{\text{table } 95\%}$ there was a 95% chance these

were **not** statistically different. This attested to the validity in the measurements and methodology. The highest differences were seen in the ethylbenzene and xylene measurements since these were the least resolved peaks.

D. Exhaust Samples

As seen in Figures 5 and 6 the BTEX compounds were in both diesel and unleaded exhaust. The car sampled for the unleaded exhaust was a 1990 *Acura Impala* and for the diesel exhaust a 2006 *VW Jetta Diesel*.

Figure 5. Exhaust Sample from a 1990 Acura Impala

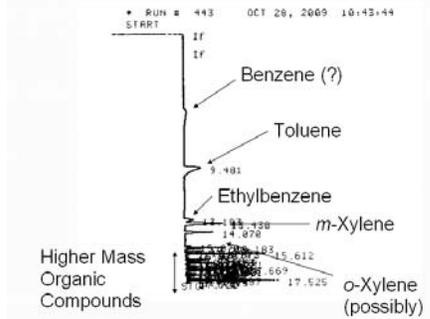
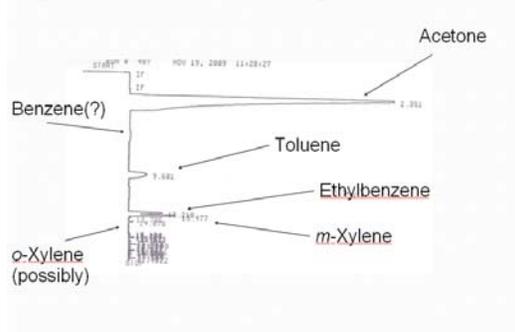


Figure 6. Exhaust Sample from a 2006 VW Jetta Diesel

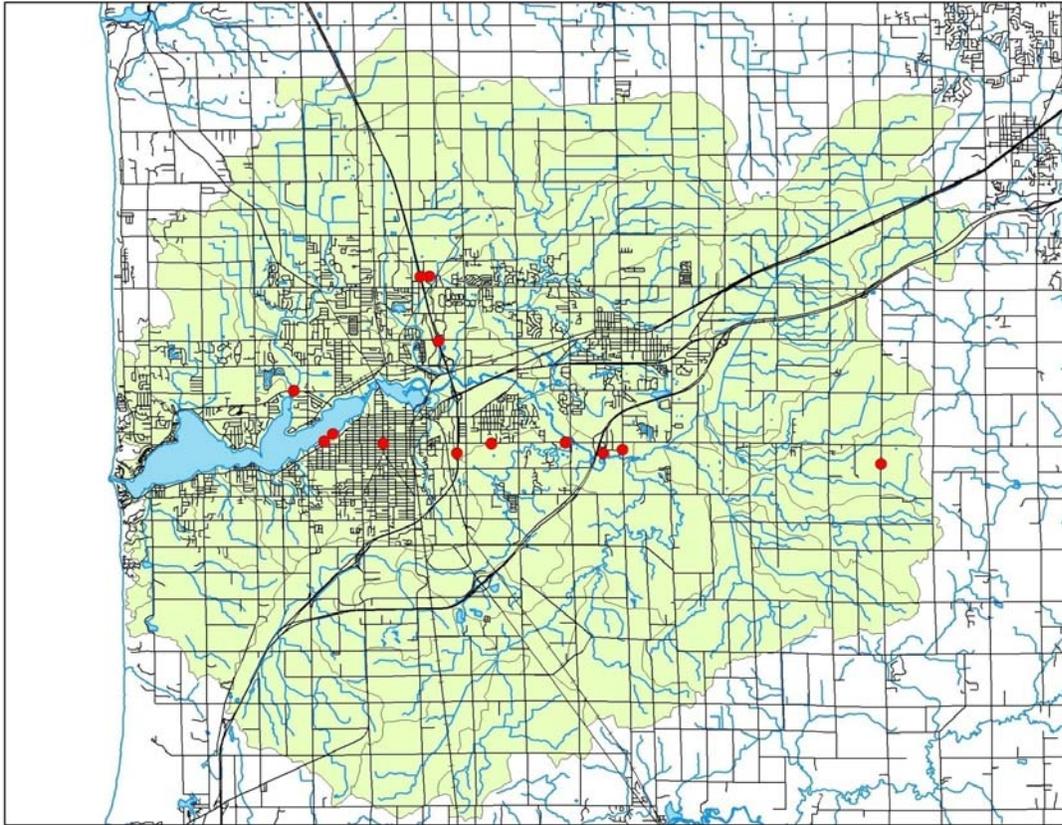


Based on these two figures (5 and 6) it was evident that BTEX compounds were being released in both diesel and unleaded exhaust.

E. Sampling Sites

A total of fourteen sites were sampled with the majority of the sites concentrated around 31 and I-196 to try and get data from high traffic locations as seen in Figure 7. A couple of sites were then chosen further away in low traffic areas as a comparison.

Figure 7. Map of Sampling Sites



The samples from each of the sites were run and the data recorded in Table 2. All the samples had BTEX levels below the detection limits except the Merchantile Bank Site. Based on the calibration curve for toluene (Figure 2), the concentration of toluene at this site was 54 ± 4 ppb. See figure 8 for the Merchantile Bank printout.

Figure 8. Merchantile Bank Printout

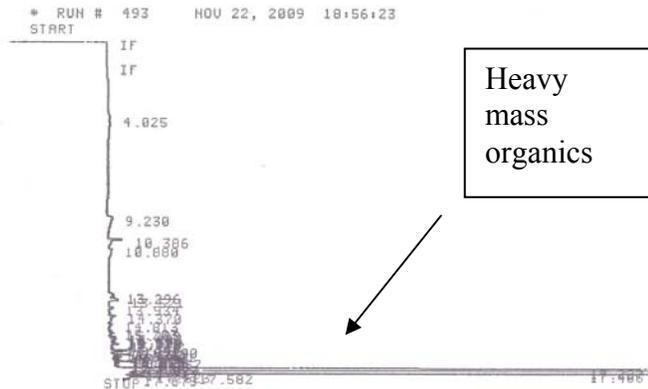


Table 2. BTEX Results for Sampling Sites

Sample Location	Benzene (ppb)	Toluene (ppb)	Ethylbenzene(ppb)	Xylene (ppb)
Queen's Inn (off 31)	<15	<10	<10	<10
Mobil Station (off 31)	<15	<10	<10	<10
Merchantile Bank (off 16th)	<15	54±4	<10	<10
Huntington Bank (off 31)	<15	<10	<10	<10
Menard's Puddle (off 16th)	<15	<3	<3	<1
Menards Pond (off 16th)	<15	<3	<3	<1
StuVisser Trails	<15	<3	<3	<1
Black River Ct. Truck Stop (off Adams)	<15	<3	<3	<1
Black River Ct. Puddle (off Adams)	<15	<3	<3	<1
Landfill (56th and Adams)	<15	<3	<3	<1
Adams St & 104	<15	<3	<3	<1
Shell Station "rain" (off River)	<15	<3	<3	<1
Shell Station puddle (off River)	<15	<3	<3	<1
Lake Mac Marina	<15	<3	<3	<1
Lake Mac (near boat launch)	<15	<3	<3	<1

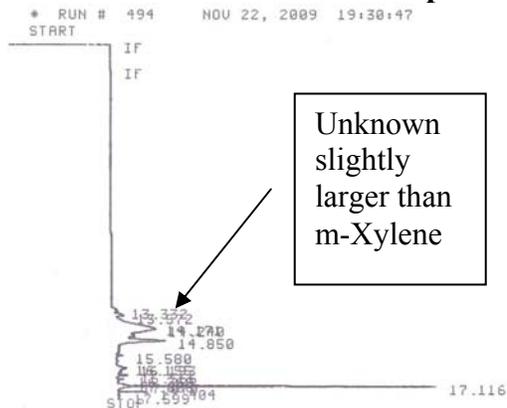
Despite not having peaks correlated to BTEX compounds, a couple of the sites had other peaks of interest. Almost all the sites had peaks in the heavier mass (non-volatile) end of the GC spectra. In addition, the samples taken at the Shell gas station had several very large peaks for higher mass organic compounds with retention times between 17 and 18 minutes. The puddle sample from this site (Figure 8) also had several smaller peaks in the volatile range with retention times slightly shifted from the BTEX times. This may have reflected a slightly altered BTEX compound, a very similar VOC or a breakdown product from a heavier compound.

Figure 9. Shell Gas Station Puddle Sample



In addition to this the Lake Macatawa site near the marina by the Heinz pickle factory had a couple of peaks pertaining to compounds slightly heavier than the BTEX compounds (See Figure 9). This site had a known fuel contamination from a leaking storage tank.

Figure 10. Lake Macatawa Marina Spectra



IV) Discussion

A large portion of this study was devoted to perfecting the sampling method, the GC parameters and calibrating the instrumentation. The result of this was the successful determination of the retention times (Table 1). The method also resulted in well-resolved peaks except for the *m*-Xylene and the Ethylbenzene.

The calibration curves were all fairly consistent with R^2 values at or above 0.96. The variation seen in the calibration data was likely due to the fact that the temperature of the water bath used to heat the samples was difficult to keep stable. The amount of component volatilizing out of the aqueous solution is dependent on the temperature so this would effect the amount of sample adhered to the needle. In addition, there was some error in the creation of the solutions. When the detection abilities of an instrument are down in the low ppb range any slight variation in solution concentration would produce a noticeable change in peak area. The detection limits were lowest (15 ppb) with the

benzene. Benzene also had the broadest, least defined peaks. This is likely a function of relative affinity of the benzene for the needle's coating.

Based on the exhaust samples BTEX compounds were clearly being emitted from the vehicles. In addition, when water was exposed to the exhaust there was a transfer of contamination from the gaseous state into the aqueous sample. While the mechanism of transfer was possible, the fact that all of the sites were below the detection limit implied that the amount present was only trace. Therefore, there was no difference observed between the samples close to busy roads and further away. Perhaps, if a more sensitive method was used such as a surge and trap column on the GC these subtle differences could have been detected.

The Merchantile bank sample that did have a fairly large toluene peak (54 ± 4 ppb) did not have any of the other BTEX compounds present. This implies that the contamination source was not likely petroleum based.

The other samples, including the one at the gas station from a puddle, did not contain any BTEX. This implies that the lightweight compounds just did not stay in the water very long. They likely volatilized out in the atmosphere fairly quickly. What was observed, however, in the samples was that most had heavier weight organics that came off the column towards the end of the run when the temperature was highest. These could not volatilize out as quickly and would be more likely to accumulate.

In the future it would be useful to identify the heavier weight organics since they seem to persist longer and accumulate more than the volatile organics. This could be done using a GC-MS. This was attempted briefly towards the end of the study but, the aqueous solutions were too dilute to get a successful extraction. It might be possible using a different solvent, multiple extractions and then a reconcentration of the extract. Other useful future studies would be to look at the effect of temperature on the levels of BTEX. This study was only done in the late fall. It would be expected that more volatile compounds would be in the water when the weather was cooler versus in the warmer summer. Also, precipitation events should affect BTEX levels. Either they would dilute any amount of contaminant present or, could carry BTEX into the watershed from spills and dribbles on the road. This could be a function of the size of the rain event with larger storms adding BTEX into the watershed but, also, flooding the water body. Smaller storms might bring in BTEX without diluting the water as much. Other possible studies could be conducted to sample actual runoff and see what level of BTEX is detected. This was briefly examined when a bottle of water was poured on a parking lot, recollected and then sampled. This came back fairly clean but, perhaps over a larger area a detectable amount of BTEX would be present.

V) Conclusion

The ultimate result of this study was that GC-FID could detect BTEX compounds down to a few ppb and that the near roadway water bodies sampled in the Macatawa watershed were predominately free of lightweight, volatile organic compounds. While the lighter weight compounds were not accumulating in the watershed almost all of the sites has several heavier organic compounds that could be good to identify in the future.

VI. References

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