"Characterization of Benzene and Other Air Toxics in Akwesasne"

St. Regis Mohawk Tribe Environment Division

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The Winds: Owera' shon: a

Let us give thanks to the winds of the earth. From the four directions they come, carrying the rains upon their back, and bringing change to the weather and the seasons. They deliver our words, and can be gentle as a whisper, or have the power of a hurricane. The winds fill us, and connect us to all life, and are the breath of the ancestors of life. The winds are the sacred breath of the Creator. Let us acknowledge the winds. So be it in your mind. Now our minds are as one.

BACKGROUND

Akwesasne, in the early years prior to being introduced to industrialization, was wealthy in regards to natural resources such as land for vegetation and livestock, clean rivers and streams for aquatic life and clean air for our people and wildlife to breathe. This way of life no longer exists since the settling of three major industrial plants, General Motors Central Foundry and two Alcoa Aluminum smelters.

Almost everything affects the air: paint and solvents evaporate; air conditioners release Freon (ozone depleting substances); cars emit combustion by-products (smog) that are released into the environment; power plants supplying electricity and manufacturing plants making products release millions of tons of pollutants into the air each year.

The Akwesasne community (US portion) consists of approximately 14,600 acres, primarily unused agricultural land and wetlands. There has been a decline in agricultural activities over the years partially due to the negative influence of industrial emissions and pollution. The rivers had also previously provided a means of income through guide fishing, and fish marketing. Since then, industrial pollution has been responsible for the contamination of the fish, to the point that government warnings have been limiting the consumption of fish.

Project Description

It is the policy of the St. Regis Mohawk Tribe to maintain a reasonable degree of purity of Tribal Air resources, which shall be consistent with the public health and welfare and the public enjoyment. The industrial development of the reservation while protecting the flora and fauna, physical property and other natural resources, require the use of all available practical and reasonable methods to prevent and manage air pollution on the reservation.

The St. Regis Mohawk Tribe's (SRMT) Air Quality Program has been in existence for 11 years. Over the years, the Program has expanded its capabilities through section 103 grants to include monitoring for criteria pollutants, indoor air education, acid rain and most recent, the development of a comprehensive Tribal Implementation Plan (TIP) for air quality. This plan outlines how the tribe plans to attain or maintain the air quality within its exterior boundaries. It is a "living document" that will be updated as new information or technology becomes available.

The SRMT Environment Division has become one of the more advanced tribal environmental programs in the country due in part to the experience gained dealing with industrial pollution.

Immediately to the west of the border of the reservation is ALCOA's St. Lawrence Reduction Plant. According to their "Notification of Continuous Release under CERCLA §103(f)," this facility releases benzene. Given the prevalence of westerly and northwesterly winds, these emissions are likely to be transported to Akwesasne on many days. Benzene is also emitted by motor vehicles and through volatilization losses from vehicle filling operations. Over the past several years Akwesasne has built up to over 15 gas stations. Exposure to benzene can

also occur with the reduction in people's homes. Gasoline is volatilized from vehicles in enclosed garages. There can also be gasoline stored for small engine operations (lawn mowers, chain saws, all terrain vehicles (ATV), and snowmobiles). Motor vehicle fuel also contains ethyl benzene, toluene, and xylenes.

Long term exposure to benzene has been shown to cause acute myelogenous leukemia. Workers are exposed to significant amounts of benzene when working with petroleum products. Most workers come into contact with benzene through inhalation and to a much lesser extent by absorbing it through their skin when working with gasoline or solvents. Community exposure to benzene from gasoline spills or fueling stations has been documented in numerous cases.

As a specific example, the Tranguch Fuel Spill was estimated to involve the leakage of 50,000-900,000 gallons of gasoline from underground storage tanks in Hazle Township and Hazleton, Pennsylvania. As a result, it is believed that residents within the remediation area were chronically exposed to low levels of benzene since at least 1990. A total of 663 individuals representing 275 households were studied. The age-adjusted standard incidence ratios (SIRs) for the Hazle Township/Hazleton affected area was 0.82 (95% CI: 0.64-1.18) for all-site cancer and was 4.12 (95% CI: 1.12-10.55) for leukemia. These results suggest a possible association between chronic low-level benzene exposure and increased risk for leukemia in the residents living near gasoline spills or fueling stations. (Patel 2004)

The air quality program through a grant from the US Environmental Protection Agency assessed the impact of benzene and other air toxics on the Akwesasne Community in conjunction with the Center for Air Resources Engineering and Science at Clarkson University. The Center for Air Resources Engineering and Science at Clarkson University partnered with the Tribe for support of instrumentation for the monitoring and sample analysis and the expertise in data analysis and modeling of this project. The Tribe's Air Quality Program was responsible for monitoring, sample/quality assurance project plans, and recruitment of individuals to participate as well as reports and budget for grant.

Project Summary

Akwesasne is located along a major state highway, state route 37, which runs directly through the territory. State Route 37 is the major artery for the North Country connecting major ports of entry to Canada as well as connecting cities and towns to the shipping industry and is heavily used by the trucking industry. The Akwesasne Mohawk Casino and other facilities attract a number of additional people to the territory and increase the volume of traffic and gasoline use. Thus, the problem is to assess the impact of the ALCOA plant on benzene concentrations across the territory relative to the ambient and personal exposure from motor vehicles and other gasoline use.

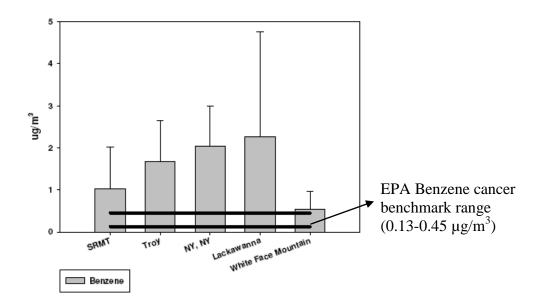


Figure 1 Comparison of the annual average benzene concentration at Akwesasne (SRMT-1.03) and other rural (WFM-0.56) and urban NY (Lackawanna-2.26, NY, NY-2.05, Troy - 1.68) monitoring sites (Aleksic, Sistla and Perry, 2005). The concentrations were obtained in 2003 except for SRMT (2007/8). The solid lines represent the EPA benzene cancer benchmark. (Units: $\mu g/m^3$)

Ambient Sampling



Figure 2.

We used NY 37 as an approximate boundary of our sampling grids as shown in Figure 3. Sampling locations were identified in each grid cell. The sampling plan called to collect a 24-hour sample every sixth day for a year using an evacuated summa canister (Figure 2.) at each sampling location.

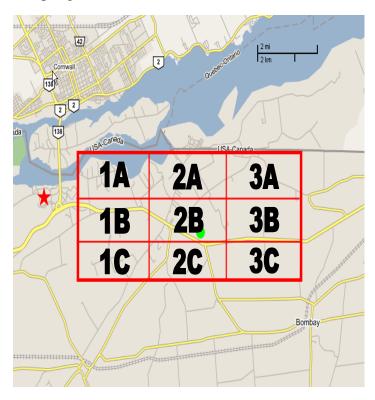
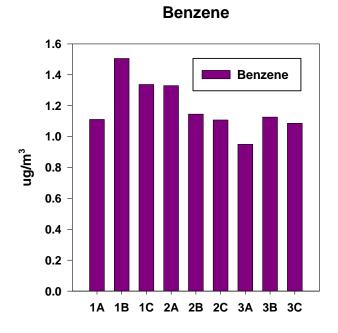


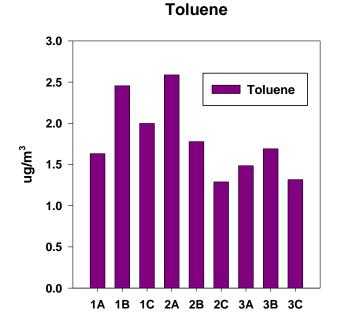
Figure 3. Map of the area showing the grid array to define the locations of the measurements relative to major benzene sources. The red star represents the reduction plant (Alcoa) and the green circle represents a casino. State route 37 runs directly through 1B, 2B, & 3B.

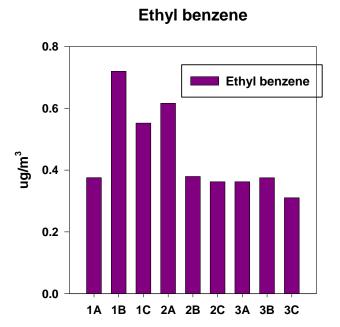
Analysis

The canisters were analyzed using approved EPA standard protocols at the facilities of the Center for Air Resources Engineering and Science at Clarkson University (CARES). A Gas Chromatograph was used to perform the analyses.

A total of 468 samples were analyzed in this study, including blanks and collocated samples. The obtained blank values were routinely low and were assumed not to influence the sample concentrations. The analytical precision for BTEX from replicate analyses of the samples and standards was within $\pm 10\%$. Fifty five collocated samples were collected and analyzed in this study. The benzene concentrations across the reservation ranged from <0.024 $\mu g/m^3$ to 12.15 $\mu g/m^3$







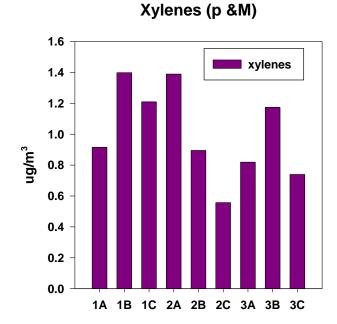


Figure 4. 45 samples Averaged from dates 07/05/05 to 05/31/08 BTEX.

The highest average Benzene and Toluene concentrations were observed at sites 1B and 2A, respectively. Sites 3A and 3C had the lowest observed BTEX concentrations. The sites are both in heavily wooded residential areas that have low traffic counts.

The annual average concentrations at site 1A were lower than expected considering the wind rose for the sampling (Figure 5). This wind rose plot shows the prevailing winds from the west and south west where 1A is downwind of the industrial emission source.

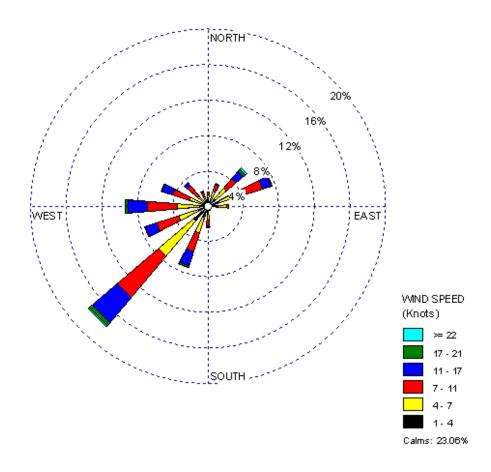


Figure 5 Wind rose plot showing the 2007 estimated annual wind direction at Massena, NY (44.9°N, 74.9 °W)

Conclusion of Ambient Samples

BTEX concentrations were obtained at all sampling sites. The overall ambient benzene concentration was 60% higher than that found in rural sampling sites in NY State. The benzene concentration was also found to exceed the EPA benzene concentration that poses a 1 in a million cancer risk by a factor of 8. Sites 2A and 1B had the highest BTEX concentrations. The seasonal average BTEX plots showed seasonal variability at all locations with high benzene concentrations during fall and winter compared to spring and summer. The low ambient temperatures coupled with decreased mixing heights during the winter and poor mixing are the probable cause of the elevated benzene concentrations during the winter months. The study shows that the benzene emissions from the neighboring aluminum smelting plant did not impact the reservation and that the sources of benzene in Akwesasne were found to be vehicle exhaust and evaporation losses from gasoline.

Source Sampling







To support the data analysis to permit the dispersal of benzene emitted by the point source relative to that emitted by mobile sources and related activities, source samples were collected and analyzed. Gasoline samples were collected periodically from multiple stations to account for the changing formulation of the fuel as a function of season. Headspace samples were obtained and analyzed using comparable methods to obtain the BETX (benzene, ethyl benzene, toluene, and xylenes) components.

The gasoline samples were collected from locally purchased gasoline from gasoline filling stations at the SRMT reservation which was collected in federally approved gasoline containers. Ten gasoline samples were analyzed namely: 6 unleaded regular (two from the same station for precision analysis), 2 unleaded midgrade and 2 unleaded premiums. These samples were purchased in December 2007, May 2008 and July 2008. The BTEX concentrations are higher in spring because the high temperatures increase evaporation losses of the VOCs in gasoline which increases exposure. Additionally, the seasonal changes in BTEX concentrations in gasoline account for the higher exposure in spring.

Table 1. Table showing BTEX concentrations obtained in December 2007

Dec-07	Benzene	Toluene	Ethyl benzene	pm Xylenes	o-Xylenes	Total
Regular	1.73	18.34	2.83	11.25	4.08	38.22
Regular	0.71	5.97	0.80	3.68	1.31	12.47
Regular *	0.98	4.70	0.60	2.65	1.00	9.93
Regular	2.14	22.17	2.14	8.31	3.61	38.36
Regular	2.03	19.32	2.58	12.00	4.02	39.95
Regular *	1.00	5.21	0.57	2.47	0.88	10.14
Average	1.43	12.62	1.59	6.73	2.48	

The regular* was obtained from the same gas station. Units % wt/wt

Table 2. Table showing BTEX concentrations obtained in May 2008

May-08	Benzene	Toluene	Ethyl benzene	pm Xylenes	o-Xylenes	Total
Regular*	1.09	12.44	2.05	9.97	3.43	28.98
Regular	1.01	12.45	1.91	9.18	3.01	27.56
Regular*	0.92	9.78	1.57	7.56	2.60	22.44
Regular	0.96	9.90	1.45	6.88	2.31	21.50
Regular	0.92	7.33	1.01	4.82	1.69	15.76
Regular	0.87	7.30	4.48	13.65	3.91	30.22
Average	0.96	9.87	2.08	8.68	2.82	

Table 3 The average concentrations of BTEX in regular unleaded gasoline December 2007, May 2008 and July 2008. The concentrations shown are wt/wt % concentrations

	Benzene	Toluene	Ethyl benzene	pm- xylenes	o-xylenes
Dec-07	1.43	12.62	1.59	6.73	2.48
May-08	0.96	9.87	2.08	8.68	2.82
Jul-08	2.45	13.39	2.51	9.28	3.39

Vehicle Emission Sampling

Tedlar bags were used to collect a series of tailpipe samples from several vehicles in each season. Three samples were collected from each vehicle, a cold start, a hot start and high speed idling at 2500rpm. The sampling was conducted on 5 days, 1 in March, 1 in April, 2 in May and 1 in June. 4 light duty vehicles, 9 vans, 3 pickup trucks and 6 off-road vehicles i.e. 2 snow mobiles and 4 all terrain vehicles (ATVs) that fuel on the reservation, all used unleaded regular gasoline and had not been driven for at least 12 hours prior to the sampling were selected in this study

Table 4. Ratios of toluene/benzene concentrations from SRMT vehicle emissions

Sampling period	Vehicle	Yr of Man.	Ratio (Tol/Bz)
Mar-08	Ford Windstar	2001	4.0
	Subaru Forester	2002	3.3
	Chevy Malibu	2004	3.5
	Chevy Trail blazer*	2004	2.8
May-08	Ford Van E250**	2000	4.0
-	Chevrolet van	2003	3.2
	Chevrolet Trail blazer*	2004	8.1
Jun-08	Ford Van E250**	2000	4.8
	Ford suburban van	2001	2.1

^{*} Repeat measurement of the same vehicle

In **Table 4**, the actual vehicle emission ratios for toluene/benzene are displayed. The toluene/benzene ratios of the older cars sampled (2001-2004) ranged from 2.8 - 4.0 in March, 3.2 - 8.1 in May and 2.1 - 4.8 in June. Comparison of the vehicle emission toluene/benzene ratios to the ambient toluene/benzene ratios shows that the average ambient ratios are lower than the ratios obtained from vehicles.

Personal Sampling

An air sampler designed by Rossner and coworkers (Rossner and Farant, 2004; Rossner et al., 2002; 2004) was used. This low sampling flow rate allows for the use of small volume canisters as personal samplers to collect benzene and other volatile organic compounds. This method allows for the collection of a whole air sampling to examine a multitude of compounds in indoor and outdoor air environments. Figure 6 presents a schematic diagram of the capillary canister. The personal capillary-canister can be used following the same TO-15 method, yet they are small enough to collect personal sample on individuals living in the Akwesasne community.

Personal samples were collected concurrently with the ambient on individuals working and living in Akwesasne. Volunteers were small 300 mL personal capillary-canisters to measure the benzene levels in the personal breathing zone of the individuals. The personal sample was collected for 6-8 hours depending upon the individual's activity patterns. Replicate samples will be collected on the same individual to obtain a range of concentrations he or she is exposed to.

Data Analysis

The locally derived profiles of evaporative gasoline and tailpipe emissions were used to calculate the amount of benzene contributed from the reduction plant. We can also use a broader spectrum of compounds measured in the source samples and EPA Chemical Mass Balance model to estimate the contributions of these two sources. Personnel at Clarkson have extensive experience in data analysis and will assist in building the capabilities for source apportionment so that it will be available for future studies.

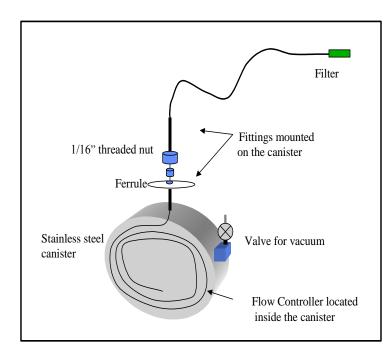


Figure 6. Capillary-Canister air sampling device. The canisters dimensions are a 300 mL stainless steel chamber 10 cm in diamter (4 inch), 2.5 cm wide (1 inch) weighing approximately 225 g (~8 oz).

Table 5.1 Personal sampling conducted at the SRMT Reservation

Sampling Date	No. of samples collected	Microenvironments sampled
03/12/2008	4 Personal / 3 Indoor	Non smoking Office, Gas stations (2), Casino (2) , Repair Shop
04/16/2008	4 Personal / 2 Indoor	Gas station (3), Gas station office, Restaurant
06/08/2008	6 Personal / 3 Indoor	Gas station (2), Gas station Office, Solid Waste, Casino, Restaurant, Daycare Center
06/16/2008	5 Personal / 4 Indoor	Gas station, Daycare Center (2) , Solid Waste, Casino(2), Restaurant, Non- smoking office
06/26/2008	4 Personal / 4 Indoor	Gas station (2), Gas station office, Casino, Daycare Center(2), Repair shop

RESULTS AND DISCUSSION

 Table 5.2 Personal Sampling Results-Benzene

Job Description/ Location	N	AM	SD	Min	Max	GM	GSD
Air technician	1	1.82	-	-	-	-	-
Casino (Indoor)	1	4.87	-	-	-	-	-
Casino	5	3.31	2.92	0.74	7.41	2.27	2.75
Daycare (Indoor)	5	0.49	0.25	0.15	0.86	0.36	1.76
Gas station	13	16.6	19.2	0.56	71.1	9.02	3.56
Gas station office (I)	3	2.07	0.52	1.47	2.40	2.02	1.32
Janitor	2	1.55	-	1.25	8.61	3.28	-
Non-smoking office (I)	2	3.54	-	0.45	6.63	1.72	-
Repair shop (Indoor)	2	11.9	-	8.53	15.2	11.40	-
Restaurant (Indoor)	3	1.17	0.39	0.72	1.45	1.11	1.46
Solid Waste	2	4.93	-	1.02	2.07	1.45	-

 Table 5.3 Personal sampling results - Toluene

Job Description/ Location	N	AM	SD	Min	Max	GM	GSD
Air technician	1	82.5	-	-	-	-	-
Casino (Indoor)	1	38.0	-	-	-	-	-
Casino	5	15.5	11.7	7.16	35.6	12.9	1.90
Daycare (Indoor)	5	8.90	3.94	4.71	13.7	7.21	1.52
Gas station	13	75.7	119	2.82	443	32.1	4.12
Gas station office (I)	3	16.0	8.39	7.80	24.6	14.4	1.78
Janitor	2	19.5	-	13.4	25.7	18.5	-
Non-smoking office (I)	2	5.41	-	4.31	6.52	5.30	-
Repair shop (Indoor)	2	224	-	41.4	407	130	-
Restaurant (Indoor)	3	4.54	3.97	1.80	9.10	3.55	2.32
Solid Waste	2	20.3	-	4.36	36.2	12.6	-

Table 5.4 Personal Sampling Results – **Ethyl benzene**

Job Description/ Location	N	AM	SD	Min	Max	GM	GSD
Air technician	1	30.5	-	-	-	-	-
Casino (Indoor)	1	1.87	-	-	-	-	-
Casino	5	2.20	1.33	0.75	4.33	1.89	1.88
Daycare (Indoor)	5	2.72	3.97	0.41	9.79	0.87	1.69
Gas station	13	9.77	13.4	0.24	47.8	3.59	5.16
Gas station office (I)	3	2.27	0.79	1.36	2.85	2.16	1.49
Janitor	2	3.02	-	1.72	4.32	2.73	-
Non-smoking office (I)	2	0.46	-	0.41	0.51	0.46	-
Repair shop (Indoor)	2	14.7	-	2.35	27.0	7.97	-
Restaurant (Indoor)	3	3.04	3.06	0.88	6.54	2.13	2.78
Solid Waste	2	2.82	-	0.39	5.25	1.42	-

Table 5.5 Personal Sampling Results - p & m Xylenes

Job Description/ Location	N	AM	SD	Min	Max	GM	GSD
Air technician	1	29.6	-	-	-	-	-
Casino (Indoor)	1	6.27	-	-	-	-	-
Casino	5	3.79	1.87	1.57	6.44	3.39	1.73
Daycare (Indoor)	5	1.78	1.44	0.55	4.26	1.08	1.60
Gas station	13	13.5	19.6	0.69	72.8	6.44	3.64
Gas station office (I)	3	2.15	1.90	0.72	4.31	1.64	2.46
Janitor	2	2.56	-	1.26	3.85	2.21	-
Non-smoking office (I)	2	1.40	-	0.96	1.83	1.33	-
Repair shop (Indoor)	2	29.1	-	8.78	49.5	20.8	-
Restaurant (Indoor)	3	1.87	0.47	1.55	2.41	1.83	1.27
Solid Waste	2	3.41	-	1.02	5.79	2.42	-

 Table 5.6 Personal Sampling Results - o-Xylenes

Job Description/ Location	N	AM	SD	Min	Max	GM	GSD
Air technician	1	20.2	-	-	-	-	-
Casino (Indoor)	1	3.04	-	-	-	-	-
Casino	5	3.77	3.48	1.26	9.90	2.91	2.12
Daycare (Indoor)	5	2.38	3.29	0.28	8.17	0.73	2.39
Gas station	13	13.1	18.1	0.25	62.7	4.52	5.60
Gas station office (I)	3	2.10	1.75	0.08	3.13	0.93	8.07
Janitor	2	8.49	-	0.55	16.4	3.00	-
Non-smoking office (I)	2	0.59	-	0.36	0.83	0.54	-
Repair shop (Indoor)	2	18.6	-	2.89	34.2	9.94	-
Restaurant (Indoor)	3	1.16	0.46	0.66	1.56	1.09	1.57
Solid Waste	2	9.93	-	0.93	18.9	4.20	-

The **Tables 5.2-5.6** summarize the personal sampling results obtained during the BTEX personal sampling campaign conducted at the SRMT reservation from March 2008- June 2008. 39 samples were evaluated in this study. While some volunteers did not wear the samplers throughout the sampling period, the canisters were analyzed the results were interpreted as full shift samples. The tables display the number of samples collected, the arithmetic (average) and geometric (normalized average) mean concentrations, minimum and maximum as well as the geometric standard. Because only one sample was obtained from the air technician and the casino (indoor), no descriptive statistics were evaluated for these. No arithmetic and geometric standard deviations were obtained for microenvironments that had less than three samples collected. High toluene concentrations are observed in all microenvironments especially in the repair shop (224µg/m³), followed by xylenes and benzene.

Toluene is considered not carcinogenic. Toluene is readily absorbed by inhalation, ingestion and through the skin. Inhaled toluene appears quickly in the brain fat (lipid) where it is rapidly eliminated. Toluene is removed rapidly from the blood. It is metabolized in the liver where it is converted via several steps primarily to hippuric acid, which is excreted in the urine. A small amount of toluene is also exhaled unchanged.

Personal Samples

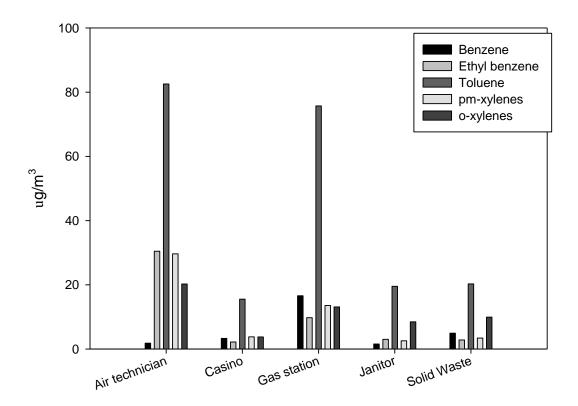
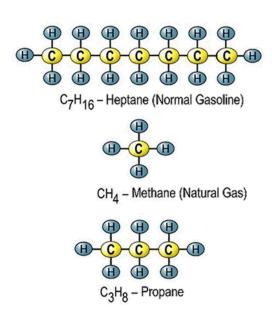


Figure 7 BTEX personal sampling average concentrations

As expected, the gas station attendants were exposed to the highest BTEX concentrations (**Figure 7**). The average benzene concentration at the gas station was $16.6\mu g/m^3$. The mean benzene concentration that the gas station attendant is exposed to is 16 times greater than the SRMT ambient benzene level. The gas stations in Akwesasne that have one gas attendant had higher BTEX concentrations compared to those that had more gas attendants. The concentrations were higher because the individual receives more exposure from the same number of vehicles. Some of the concentrations from the gas stations especially on 04/16/2008 ($0.56\mu g/m^3$) were low because the samplers were not worn throughout the sampling period. The sampler was worn for about an hour. The gas attendants reported that the work activities included filling cars ~ 15-20 vehicles/hour, mowing lawns and sweeping the parking lot. The sources of BTEX that increased exposure at the gas stations included volatilization of gasoline from the gas tanks, volatilization losses during refueling as well as emissions from the lawn mowers and vehicles that fuel at the gas station. In an EPA mobile sources air toxics study (EPA 2007a), the current average level of benzene in gasoline in the United States was reported as 1.0% by volume and the fraction of benzene in the exhaust of on-road vehicles was 3-5%.

Conclusion



The SRMT Environment Division secured funds through a grant from the US EPA to conduct a study on Benzene exposure of the community. The reason this was done was because of the continuous release of Benzene from a neighboring industry. This study measured Benzene, Toluene, Ethyl Benzene and Xylenes (o and m & p).

The results of the study show that the primary exposure of Benzene (the chemical of concern) was from vehicle exhaust and fueling stations. Benzene is very volatile, which means it evaporates readily at normal temperatures and pressures so exposure would come from a more localized source.

Acknowledgements

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Niawen!