

A STUDY TO QUANTIFY ON-ROAD EMISSIONS OF DIOXINS AND FURANS FROM MOBILE SOURCES: PHASE 2

Health and Environmental Sciences Department
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A Study to Quantify On-Road Emissions of Dioxins and Furans from Mobile Sources: Phase 2

Health and Environmental Sciences Department

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ABSTRACT

This report describes the results of a study of the on-road emissions of dioxins and furans from mobile sources. This work was done in response to the US EPA's draft Dioxin Reassessment document which used data from sources outside the US to estimate an emission factor for the US fleet. The EPA estimate for dioxin emissions from the heavy-duty fleet was 0.8 ng/mile expressed in terms of TEQ or Toxicity Equivalents (a set of factors intended to adjust concentrations based on relative toxicity). The primary objective of this work was to develop on-road chlorinated dioxin and furan emission factors for in-use vehicles operating in the US with particular emphasis on heavy-duty vehicles. The experimental approach was to measure emissions in the Fort McHenry Tunnel, Baltimore, Maryland. All air entering and leaving the tunnel was sampled for concentrations of dioxins and furans (during ten sampling periods of 24 hours each). The difference between the mass of material entering and the mass of material leaving the tunnel was taken to be the amount produced by the vehicles in transit. These measurements were combined with information on vehicle counts (obtained through videotapes) and tunnel length to determine an average emission factor. The study was conducted from October 25 to November 6, 1995. The average heavy-duty diesel emission factor determined in this study was 0.28 ng TEQ/mile.



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EXECUTIVE SUMMARY

This report describes the results of Phase 2 of "A Study To Quantify On-Road Emissions Of Dioxins From Mobile Sources." This builds upon the results of the Phase 1 study in which preliminary measurements were made in the Van Nuys Tunnel to verify application of the dioxin and furan collection and analytical methods to tunnel conditions and to develop recommendations for a more complete experiment. Phase 2 continued this work while focusing on emissions from heavy-duty diesel vehicles and consisted of measurements of dioxin and furan emissions in the Fort McHenry Tunnel.

Background

In a recent draft Dioxin Reassessment document, the US EPA reports estimated dioxin and furan emission factors from mobile sources. The EPA estimated dioxin emission factor for the heavy-duty fleet was 0.8 ng/mile expressed in terms of TEQ or Toxicity Equivalents (a set of factors intended to adjust concentrations of various chlorinated dioxins and furans based on relative toxicity). This estimate was primarily based on studies conducted outside the US, including one on-road study done in a tunnel in Norway. The EPA report also presents evidence that light-duty and heavy-duty diesel vehicles are sources of dioxins and furans based on dynamometer tests and muffler scrapings. While there is little doubt that motor vehicles are sources of dioxins and furans, the magnitude of these emissions is uncertain. The application of the Norwegian results, which were confounded by a light-duty fleet operating on leaded gasoline, to the US fleet has also been criticized and the US EPA has indicated additional research is needed.

The approach supported by EPA to address this question is to perform engine dynamometer tests of heavy-duty diesel emissions. An alternative approach to determine mobile source emissions of dioxins and furans, applied in this study, is to perform an on-road experiment in a roadway tunnel to determine emission factors. While this method does not permit the same degree of control over operating conditions as could be obtained in a dynamometer study (fuel, load, etc.) it does enable one to quantify emissions from the in-use fleet.

Results of Phase 1

Prior to performing this experiment, an initial study (Phase 1) was undertaken in June 1995 in the Van Nuys Tunnel (Sherman Way under the Van Nuys Airport, Van Nuys, California). The objectives of Phase 1 were to lay the groundwork for a more complete experiment, to verify application of the dioxin and furan collection and analytical methods to tunnel conditions, and to assess the ability of the current tunnel methodology to determine mass emission rates for dioxins and furans.

The Phase 1 study showed that the methodology employed for determining mass emissions of various pollutants in roadway tunnels was applicable to the

study of dioxins and furans from mobile sources. It also provided the basis for several changes in the experimental procedure for Phase 2 to improve the capability of detecting and measuring dioxin and furan emissions at the lowest levels feasible. These were:

- Increasing the sampler flow rate by a factor of 2.
- Increasing the sample duration from 12 to 24 hours.
- Changing to a day/day and a night/night sampling schedule to examine cases which maximize traffic count and thus concentration (day/day) and maximize the fraction of heavy-duty vehicles (night/night).

These steps were designed to increase measurement sensitivity and enable calculation of emission factors of <0.075 ng-TEQ/mile.

Objectives of Phase 2

The primary objective of this work was to develop on-road emission factors for chlorinated dioxins and furans from in-use vehicles operating in the US. The approach taken was to measure mobile source emissions in a tunnel — the same methodology as was previously applied in tunnel studies to measure regulated gaseous emissions from mobile sources.

As part of this work answers were sought for the following questions:

- Are heavy-duty dioxin emission factors from the US fleet as high as those observed in the Norwegian study?
- How do emission factors for heavy-duty and light-duty vehicles that are calculated from US roadway tunnel measurements compare with current EPA estimates?
- Is resuspended road dust a significant source of the observed dioxin emissions?

Experimental Description

The Fort McHenry Tunnel is a four-bore tunnel, two lanes per bore, carrying Interstate 95 east-west traffic under the Baltimore Harbor. The downgrade reaches -3.76% and the upgrade reaches +3.76%, with no significant level portion. Average grade from west portal to bottom is -1.8% and, from bottom to east portal, +3.3%. The tunnel's four bores are designated 1 and 2 westbound (towards Washington, DC), and 3 and 4 eastbound (towards Philadelphia, PA). This study was performed in Bores 3 and 4, the eastbound bores (length 2174 meters). Light-duty vehicles are allowed in both bores, while trucks are directed into Bore 4, the right-hand bore. The fleet in Bore 3 generally contained less than 2% heavy-duty diesel vehicles, while Bore 4 contained on average 24 to 25% heavy-duty diesel vehicles during the course of this experiment. Posted speed was 50 mi/hr in the tunnel, 55 outside. Traffic flowed freely except for sporadic light braking/slowdown at the exit at rush hour.

The ventilation system of the Fort McHenry Tunnel comprises two sections. Ventilation air, drawn in through the ventilation buildings, is supplied through

ducts beneath the roadway, and tunnel air can be removed through overhead exhaust ducts. During this experiment, the exhaust fans were shut off. In this situation, typically 10% of the air comes in through the east supply duct, 10% through the west supply duct, and 80% through the west portal. Actual tunnel flow volumes were determined in each run from anemometer measurements and known cross sections in the tunnel. Air flows through the supply ducts were determined from the stated fan ratings reported by the Tunnel Operations. All of the air leaves through the tunnel exit portal. Flow balances (in vs. out) were within $\pm 9\%$, on average.

The Fort McHenry Tunnel is generally very well maintained and very clean relative to other tunnels. The Tunnel maintenance personnel cleaned the tunnels (a process which includes cleaning the walls in addition to street-sweeping) the weekend of the 22nd and 23rd of October, 1995, which is the weekend before this study began.

Sampling Stations

Sampling stations were set up at six locations: one each at the supply (air intake) for the ventilation air at the west and east ventilation buildings, one each on the catwalk in bores 3 and 4 at the west (entrance) end of the tunnel, and one each on the catwalk in bores 3 and 4 at the east (exit) end of the tunnel.

At each of the air intakes there was a high volume dioxin sampler and a sampler for particles less than 10 μm in aerodynamic diameter (PM_{10}).

At each entrance roadway station there was a propeller anemometer for air flow, a high volume dioxin sampler, and, in Bore 4 only, a PM_{10} sampler.

At each exit roadway station there was a propeller anemometer for air flow, a high volume dioxin sampler and, in Bore 4 only, a PM_{10} sampler. Starting with the 3rd sampling period a second high volume dioxin sampler was added at the Bore 4 site to increase the amount of sample collected at this important site. The samples from the two dioxin samplers were combined and analyzed as one.

A video camera was placed at each exit station and video tapes from the cameras were used to determine vehicle counts and traffic composition.

Run Descriptions

A total of 15 runs during the 10 sampling periods were performed in the two bores. There were 5 daytime experiments performed in Bores 3 and 4 (10 runs total) and 5 nighttime runs performed only in Bore 4 (5 total runs). Day runs commenced at 0600 and ended at approximately 1800. Night runs began at 1800 and ended at approximately 0600 the next day. End times are approximate since time was required to change out the sample media for the dioxin samplers.

No speed data were recorded as part of this study. Based on previous Fort McHenry work speeds were on the order of 50 mi/hr with the entering traffic slightly higher and the exiting (uphill) traffic slightly slower.

Bore 3 contained, on average 1.9% heavy-duty vehicles, while Bore 4 contained 24.2% heavy-duty vehicles. The fraction of heavy-duty vehicles in Bore 4 was similar for the day and night periods — 24.0% and 24.8%, respectively. Daytime vehicle counts in Bore 4 were 2.25 times greater than the nighttime counts. Bore 4 and Bore 3 daytime vehicle counts were, on average, within 10% of each other.

Results and Conclusions

The results of the chemical analyses were tabulated and validated, and emission factors were calculated for each run period. For Bore 3, the difference between the outlet and inlet concentrations was too small to accurately estimate emission factors. This precluded directly separating the light-duty component from the Bore 4 results to obtain heavy-duty diesel emission factors. Given the large fraction of heavy-duty diesel vehicles in Bore 4 and the assumption that heavy-duty diesel dioxin and furan emissions are significantly greater than light-duty dioxin and furan emissions, all observed emissions in Bore 4 were attributed to the heavy-duty diesel fleet. This means the resulting estimate will be an upper bound for the actual emission factor. The average for the 7 valid runs in Bore 4 was 0.28 ± 0.13 ng-TEQ/mile.

These results are lower than the EPA estimate of 0.8 ng-TEQ/mile. Possible explanations for the difference may be because the EPA estimate is based in part on a Norwegian study, where:

- The heavy-duty diesel fraction in the Norwegian study was between 3 and 15% of the total fleet and the results were extrapolated to 100% heavy-duty diesel.
- The light-duty fleet in the Norwegian study was operating using leaded fuel, a source of dioxins and furans.
- There are likely to be technology and fuel differences between Norwegian and US heavy-duty diesel vehicles.
- It is possible there were differences in load on the vehicles in the two studies.

Emission profiles were also compared with the results of German dynamometer tests. Given the differences in the tests, the results were in good agreement.

PM₁₀ emission factors were also estimated as part of this work. The observed heavy-duty diesel emission factor of 0.32 ± 0.11 g/mile was lower than the 0.54 ± 0.12 g/mile observed in a study in the Fort McHenry Tunnel in 1993. Although the results agree to within the experimental uncertainty, possible reasons for the apparent difference may be due to the shorter run periods (1-hr.) and the dominance of 5 high emission factor runs in the 1993 study.

Chemical Mass Balance (CMB) modeling was conducted on the Bore 4 outlet PM₁₀ filters. Resuspended road dust was found to account for 15.5 ± 3.3 % of the measured mass. The contribution from resuspended road dust to the observed dioxin and furan emission factors was estimated to be approximately 4%, calculated by incorporating the measured concentrations of dioxins and

furans in collected road dust. Results of the inorganic analyses were also used to determine the impact of ambient PM_{10} chlorine levels on dioxin and furan mass emission factors. An analysis of these data indicated there was no correlation between ambient PM_{10} chlorine and dioxin and furan emissions.

1.0 INTRODUCTION

This report describes the results of Phase 2 of "A Study To Quantify On-Road Emissions Of Dioxins From Mobile Sources." This builds upon the results of the Phase 1 study (Gertler *et al.*, 1995a) in which preliminary measurements were made in the Van Nuys Tunnel to verify application of the dioxin and furan collection and analytical methods to tunnel conditions and to develop recommendations for a more complete experiment. Phase 2 emphasized studying emissions from heavy-duty diesel (HDD) vehicles and consisted of measurements of dioxin and furan emissions in the Fort McHenry Tunnel (Baltimore, Maryland).

1.1 Background

In a draft report entitled "Estimating Exposure to Dioxin-Like Compounds" (EPA, 1994a) the EPA reports estimated dioxin and furan emission factors from mobile sources. The EPA estimated dioxin emission factor for HDD vehicles was 0.8 ng-TEQ¹/veh-mi. To arrive at this value the EPA used several values, including a study of the Norwegian fleet by Oehme *et al.* (1991), which reported HDD dioxin and furan emission factors of 5.1 ng-TEQ/km (or 8.2 ng-TEQ/veh-mi). The Norwegian value was derived from the average of emissions measurements made in both the uphill and the downhill directions of a highway tunnel.

The report also presents evidence that light-duty (LD) and HDD vehicles are sources of dioxins and furans based on dynamometer tests and muffler scrapings. The magnitude of dioxin and furan emissions from motor vehicles is uncertain. The application of the results from Oehme *et al.* to the US fleet has also been criticized (Unsworth, 1994) and the US EPA has indicated additional research is needed.

The approach supported by EPA to address this question is to perform engine dynamometer tests of HDD emissions. An alternative approach to determine mobile source emissions of dioxins and furans, applied in this study, is to perform an on-road experiment in a roadway tunnel to determine emission factors. While this method does not permit the same degree of control over operating conditions as could be obtained in a dynamometer study (fuel, load, etc.) it does enable one to quantify emissions from the in-use fleet.

1.2 Results of Phase 1

Prior to performing this experiment, an initial study (Phase 1) was undertaken in June 1995 in the Van Nuys Tunnel (Sherman Way under the Van Nuys Airport, Van Nuys, California). The objectives of Phase 1 were to lay the groundwork for a more complete experiment, to verify application of the dioxin and furan collection and analytical

¹ 2,3,7,8-TCDD toxicity equivalents. A series of factors intended to adjust concentrations of other dioxin isomers to equivalent concentrations of 2,3,7,8-TCDD, based on relative toxicity.

methods to tunnel conditions, and to assess the ability of the current tunnel methodology to determine mass emission rates for dioxins and furans.

The Phase 1 study showed that the tunnel methodology employed for determining mass emissions of various pollutants was applicable to the study of dioxins and furans from mobile sources. It also provided the basis for several changes to experimental procedures for Phase 2 to improve the capability of detecting and measuring dioxin and furan emissions at the lowest levels feasible. However, it also demonstrated the limitations in detecting the low level of emissions from these sources (Gertler *et al.*, 1995a). The Van Nuys experiment was not an ideal case: the tunnel was relatively short (222 m), the traffic volumes were fairly low and the traffic composition was nearly completely light-duty. This did not allow for estimation of HDD emissions. In addition, most species were below the analytical detection limit for the 12-hr. sampling periods. Given these limitations, absolute emission factors could not be calculated. Upper limits for mass and TEQ emission factors were made assuming the non-detected species at the tunnel outlet were present at their detection limits and the inlet concentrations were zero. For the mixed fleet observed in Van Nuys (approximately 99% light-duty), the upper limit mass emission factor for all isomers was <0.3 ng/veh-mi and the TEQ emission factor was <0.03 ng-TEQ/veh-mi.

Based on the Phase 1 study, our previous work in Fort McHenry (Pierson *et al.*, 1996), and the assumption that all species may be below the detection limit, estimated HDD detection limits in Fort McHenry were <7.5 ng/veh-mi and <0.3 ng-TEQ/veh-mi. In order to lower these limits in the Phase 2 study, we proposed several experimental changes to improve our ability to determine emission factors. These were:

- Increasing the sampler flow rate by a factor of 2.
- Increasing the sample duration from 12 to 24 hours.
- Change to a day/day sampling schedule in Bores 3 and 4 and a night/night sampling schedule in Bore 4 to look at cases where we have the maximum traffic count and thus concentration (day/day) and maximum fraction of HDD vehicles (night/night).

We estimated these steps should increase our measurement sensitivity and enable us to develop upper limit emission factors of <1.9 ng/veh-mi and <0.075 ng TEQ/veh-mi.

1.3 Objectives

The primary objective of this work was to develop on-road dioxin and furan emission factors from in-use vehicles operating in the US. The approach taken was to measure mobile source emissions in a tunnel employing the same methodology applied in previous tunnel studies to quantify CO, NMHC, NO_x, and CO₂ emissions from mobile sources (e.g., Pierson *et al.*, 1990, 1996).

As part of this work we attempted to answer the following questions:

- Are HDD dioxin emission factors from the US fleet as high as those observed in the earlier Norwegian study?
- How do measured emission factors for HDD and LD vehicles compare with current EPA estimates?

- Is resuspended road dust a significant source of the observed dioxin emissions?

Initially we had planned to assess downhill vs. uphill emission factors by placing a sampler at the low point of the tunnel, near the air handling bulkhead (see Section 2.1). However, due to safety concerns, the Tunnel Authority did not allow sampling at this location so this objective had to be dropped. This change did, however, make an additional sampler available that was collocated with the other sampler at the Bore 4 exit to increase the sample collected there.

We had also planned on measuring the light-duty emissions in Bore 3 and subtracting this value from that determined in Bore 4 to calculate a heavy-duty only emission factor. However, the Bore 3 emissions were too low to estimate with this methodology (see Section 4.2), so we calculated heavy-duty emission factors by assuming that all emissions of dioxins and furans came from heavy-duty vehicles. This approximation will result in an over-estimate of the heavy-duty emission factor.

1.4 Guide to Report

This first section has provided the background on the project, summarized the Phase 1 results and recommendations, and outlined the objectives of the current study. Section 2 contains a description of the Fort McHenry Tunnel and outlines the sampling runs and vehicle counts. Section 3 details the experimental methods used to perform the study. The results for the dioxin and furan emissions and a comparison with previous studies are presented in Section 4. PM_{10} emission factors and an estimate of resuspended road dust to the observed emission factors are reported in Section 5. Section 6 contains the summary, and all references for the report are listed in the References section. The Appendices contain all analytical results and calculated concentrations for cases where only summary tables are provided in the main body of the text as well as all tunnel volumetric flows by run.

2.0 EXPERIMENTAL DESCRIPTION

In this section, we briefly describe the physical layout of the Fort McHenry Tunnel and present run descriptions of the sampling periods.

2.1 Tunnel Description

The Fort McHenry Tunnel (Figure 2-1) is a four-bore tunnel, two lanes per bore, carrying Interstate 95 east-west under the Baltimore Harbor. The downgrade reaches -3.76% and the upgrade reaches $+3.76\%$, with no significant level portion. Average grade from west portal to bottom is -1.8% and, from bottom to east portal, $+3.3\%$. The tunnel has four bores (Figure 2-2), designated 1 and 2 westbound (towards Washington, DC), and 3 and 4 eastbound (towards Philadelphia). This study was performed in Bores 3 and 4, the eastbound bores (length 2174 meters). LD vehicles are allowed in both bores. Trucks are directed into Bore 4, the right-hand bore. The fleet in Bore 3 generally contained less than 2% HDD vehicles, while Bore 4 contained on average 24-25% HDD vehicles. Posted speed was 50 mi/hr in the tunnel, 55 outside. Traffic flowed freely except for sporadic light braking/slowdown at the exit at rush hour.

The ventilation system of the Fort McHenry Tunnel comprises two sections. Ventilation air, drawn in through the ventilation buildings (Figure 2-1), is supplied through ducts beneath the roadway, and tunnel air can be removed through overhead exhaust ducts. During this experiment, the exhaust fans were shut off. In this situation, typically 10% of the air comes in through the east supply duct, 10% through the west supply duct, and 80% through the west portal. Actual tunnel flow volumes were determined in each run from anemometer measurements and known cross sections in the tunnel. Air flows through the supply ducts were determined from the stated fan ratings reported by the Tunnel Operations. All of the air leaves through the tunnel exit portal. Flow balances (in vs. out) were within $\pm 9\%$, on average. All reported and measured air flows are in Appendix 4.

There is a bulkhead in the ventilation ducts 95 meters before (i.e., west of) the low point of the tunnel. This bulkhead effectively separates the tunnel into west and east sections. The west ventilation section contains 93% of the downhill travel while the east section contains the rest of the downhill and all of the uphill. We had hoped to sample at the dividing bulkhead to allow determination of downhill vs. uphill emission factors; however, this was dropped because the Fort McHenry Tunnel Authority would not allow samplers to be placed near the bulkhead due to safety concerns.

The Fort McHenry Tunnel is generally very well maintained and very clean relative to other tunnels. The Tunnel maintenance personnel cleaned the tunnels (a process which includes cleaning the walls in addition to street-sweeping) the weekend of the 22nd and 23rd of October, 1995, which is the weekend before we began sampling.

2.2 Sampling Stations

Sampling stations were set up at six locations: one each at the supply (air intake) for the ventilation air at the west and east ventilation buildings, one each on the catwalk in bores 3 and 4 at the west (entrance) end of the tunnel, and one each on the catwalk in bores 3 and 4 at the east (exit) end of the tunnel.

At each of the supply (air intake) stations for the ventilation air there was a high volume dioxin sampler and a sampler for particles less than 10 μm aerodynamic diameter (PM_{10}).

At each west (entrance) roadway station there was a propeller anemometer for air flow, a high volume dioxin sampler, and, in Bore 4 only, a PM_{10} sampler.

At each east (exit) roadway station there was a propeller anemometer for air flow, a high volume dioxin sampler and, in Bore 4 only, a PM_{10} sampler. Starting with the 3rd sampling period (0600 on 27 October 1995), a second high volume dioxin sampler was added at the Bore 4 site. The samples from the two dioxin samplers were combined and analyzed as one.

Also at each east station there was a small black-and-white video camera aimed to be able to see the tunnel traffic. The signals from both video cameras were merged by a screen splitter and recorded, along with the date and time, on a long-play video recorder that can record 24 hours on a single tape. These video tapes were used to determine vehicle counts and traffic composition.

2.3 Run Descriptions

Descriptions of the 10 sampling periods are contained in Table 2-1. A total of 15 runs was performed in the two bores. There were 5 daytime experiments performed in Bores 3 and 4 (10 runs total) and 5 nighttime runs performed only in Bore 4 (5 total runs). Day runs commenced at 0600 and ended at approximately 1800. Night runs began at 1800 and ended at approximately 0600 the next day. End times are approximate since time was required to change out the polyurethane foam (PUF) and filter media for the dioxin samplers.

Weather observations during sampling runs are also recorded on Table 2-1. Since each run consisted of two 12-hour periods separated by at least another 12 hours, the weather observations for the two separate periods are presented. The temperature data are the highest and lowest recorded values for that period, based on hourly observations, and the sky conditions are those observed by the National Weather Service office at the Baltimore-Washington Airport.

No speed data were recorded as part of this study. Based on our previous Fort McHenry work (Pierson *et al.*, 1996) speeds were on the order of 50 mi/hr with the entering traffic slightly higher and the exiting (uphill) traffic slightly slower.

Bore 3 contained, on average 1.9% HD vehicles, while Bore 4 contained 24.2% HD vehicles. The fraction of HD vehicles in Bore 4 was similar for the day and night periods — 24.0% and 24.8%, respectively. Daytime vehicle counts in Bore 4 were 2.25 times greater than the nighttime counts. Bore 4 and Bore 3 daytime vehicle counts were, on average, within 10% of each other.

Figure 2-1. Cross Sectional View, Fort McHenry Tunnel

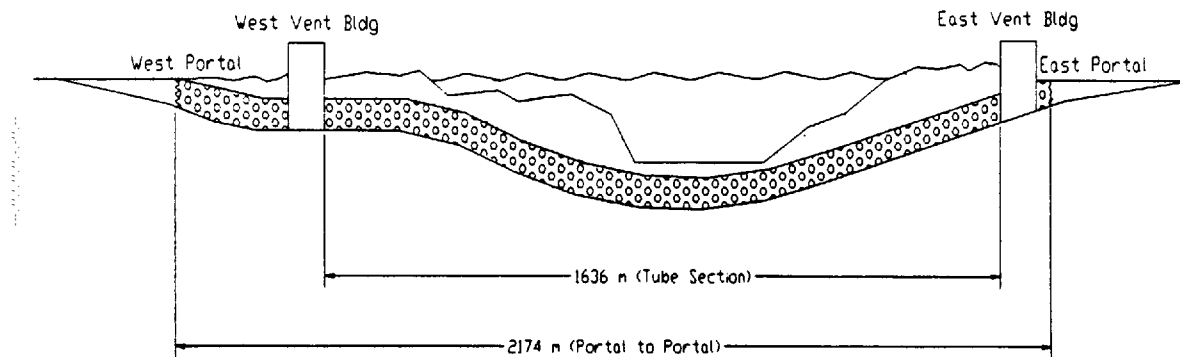


Figure 2-2. Cross Sectional View of Bores, Fort McHenry Tunnel

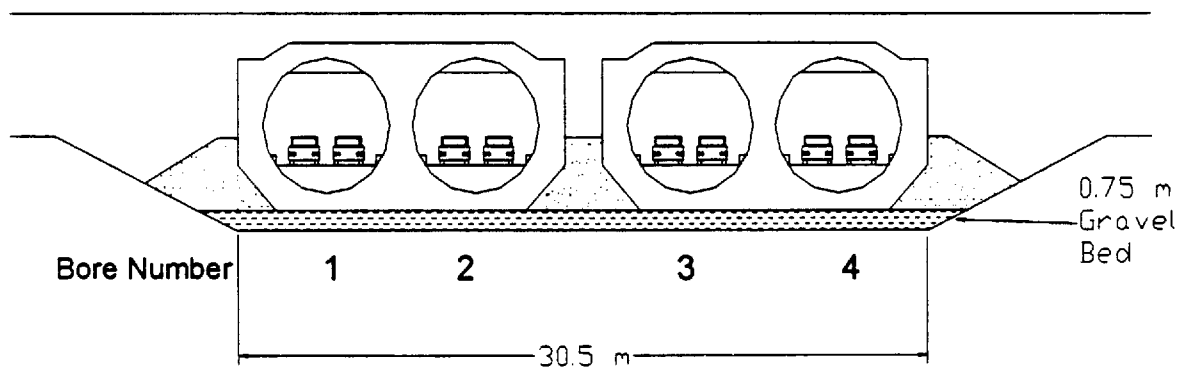


Table 2-1. Run Descriptions, Fort McHenry Tunnel. Weather observations show range of temperatures and sky conditions.

Run	1	2	3	4	5	6	7	8	9	10	AVG.
Start Date	25-Oct	25-Oct	27-Oct	27-Oct	31-Oct	31-Oct	2-Nov	2-Nov	6-Nov	6-Nov	
Day	Wed/Thur	Wed/Thur	Fri/Mon	Fri/Mon	Tues/Wed	Tues/Wed	Thur/Fri	Thur/Fri	Mon/Tues	Mon/Tues	
Start Time: Day 1	600	1800	600	1800	600	1800	600	1800	600	1800	
Start Time: Day 2	600	1800	600	1800	600	1800	600	1800	600	1800	
Total Vehicles: Bore 3	34,468		36,554		28,015		35,214		15,910		30,032
LD: Bore 3	33,858		35,897		27,474		34,432		15,625		29,457
HD: Bore 3	610		657		541		782		285		575
Total Vehicles: Bore 4	33,668	13,128	36,173	18,404	38,578	10,548	16,719	14,164	16,876	6,824	20,508
LD: Bore 4	24,774	10,346	28,228	15,076	29,842	6,959	12,285	10,088	12,789	4,957	15,534
HD: Bore 4	8,894	2,782	7,945	3,328	8,736	3,589	4,434	4,076	4,087	1,867	4,974
% HD: Bore 3	1.8%	--	1.8%	--	1.9%	--	2.2%	--	1.8%	--	1.9%
% HD: Bore 4	26.4%	21.2%	22.0%	18.1%	22.6%	34.0%	26.5%	28.8%	24.2%	27.4%	24.3%
Weather Observations											
Temps: Day 1 (°F)	53-60	40-57	52-68	61-67	48-60	53-56	65-68	65-64	32-51	34-40	
Temps: Day 2 (°F)	40-60	44-59	42-62	47-52	58-61	61-63	58-73	37-58	38-49	40-49	
Weather: Day 1	Clear	Pt. Cloud	Overcast	Rain	Overcast	Overcast	Fog/Rain	Rain/Cloud	Clear/Scat.	Scat Cld	
Weather: Day 2	Fog	Cloud/Fog	Scat. Cld	Scat. Cld	Rain/Fog	Fog/drizzle	Overcast	Clear/Scat.	Cloud/Rain	Overcast	

3.0 EXPERIMENTAL METHODS

In this section we describe the measurement and dioxin and furan analytical methods along with the methodology for calculating emission factors in tunnels. PM₁₀ analytical methods are detailed in Section 5.

3.1 Measurement Methods

As described in the previous section, sampling stations were required at six locations: Two at the west portal (tunnel entrance), one at east supply, one at west supply, and two at the east portal (tunnel exit). At each sampling location there was a propeller anemometer for air flow measurements and high volume sampler for collection of dioxins and furans. PM₁₀ samplers were also located in the two supplies and Bore 4 inlet and outlet to collect size fractionated particulate matter.

The anemometers used were RM Young Model 05103, interfaced to a Campbell 21x datalogger. The flow measurements were recorded in Campbell battery-backed memory modules and downloaded to a computer once each week and at the end of the study.

The PM₁₀ samples were collected using DRI medium-volume PM₁₀ samplers designed to collect samples for chemical analysis (Gertler *et al.*, 1993). This type of sampler employs a Sierra-Andersen 254 PM₁₀ inlet to collect only those particles with aerodynamic diameters less than 10 µm. The ambient air is transmitted through the size-selective inlet and into a plenum. The flow rate is controlled by maintaining a constant pressure across a valve with a differential pressure regulator. For the size selective inlet to work properly, a flow rate of 113 liters per minute (lpm) must be maintained through the sampler. Flow rates of 20 lpm through each filter are standard for these studies because they generally provide adequate sample loadings for analysis without overloading the filters. This flow rate is drawn simultaneously through two parallel filter packs, one with a Teflon® substrate (for mass and metals) and one with a quartz substrate (for carbon and ions). The remaining 73 lpm are drawn through a makeup air port. The flow rates are each set with calibration filters and calibrated rotameter and are monitored with the same rotameter at each sample change.

Dioxins and furans were collected using Graseby GMW Model GPS1 PUF samplers. The sampler does not have a size-selective inlet, but does have a shelter top to prevent exposure of the media to material falling on it. It is thus a total suspended particles (TSP) collection process. The actual sampling train consists of a 10 cm glass fiber filter backed up by a cartridge of polyurethane foam (PUF). Samplers were calibrated with a calibrated orifice (Graseby GMW Model G40) prior to the beginning of the study.

In order to maximize the amount of sample collected for dioxin analysis, runs were scheduled on a day/day and night/night basis to yield a 24-hr. sampling period. Dioxin sampler flows were also maximized to approximately 24 standard cubic feet per minute (scfm) to increase sample collection. Flows in the Bore 4 outlet dioxin sampler had to be reduced to approximately 19 scfm in order to reduce clogging of the media and the concurrent severe reduction in sampler flow. In order to compensate for this problem, samplers were collocated at the Bore 4 outlet beginning with Run 3 and the collected

samples were combined for analysis. Even with the collocated samples, these samplers experienced considerable loading and the flow rates dropped over the sample periods. To compensate for this, after the first 12 hour sample period the flow was readjusted back up to the starting value for the second 12 hour period. Total volume collected was the sum of the two 12 hour periods, and for each period we used the average of the start and end flows to calculate the volume sampled. Flow data was not monitored continuously. Based on DRI's previous experience with this type of sampler, an error of $\pm 5\%$ is expected on the total volume calculated.

3.2 Dioxin and Furan Laboratory Methods

Following sampling, the filters and PUF media were shipped to Quanterra Environmental Services, Inc. (Sacramento, California) for analysis. Shipments were made by overnight carrier and the samples were packed in coolers with blue-ice packs to keep the samples cool. The general sampling and analysis approach followed was that of US EPA Method TO-9 (EPA, 1988), but employing the analytical improvements of Method 8290 (EPA, 1994b). Method TO-9 describes the air sampling protocol, including pre-cleaning of media and extraction and analysis for only four dioxins and no furans. Method 8290 is an analytical method only that expands the list of target compounds to include the full range of dioxin and furan congeners. As part of method 8290 samples are extracted, cleaned up and subjected to high resolution gas chromatography/high resolution mass spectrometry for identification and quantification of tetra- through octa-chlorinated dioxins and furans. The method allows for ppt and sub-ppt determination of 2,3,7,8-substituted PCDD/PCDF isomers.

3.2.1 Dioxin/Furan Method Summary

PUF and Filter Cleaning Procedures

PUFs and filters are subjected to a 16 hour soxhlet extraction with 200-300 ml of toluene. PUFs and filters are removed from the soxhlets and allowed to air dry in a hood until all traces of solvent have dissipated. After this first phase is complete a set of PUFs is selected from the batch to determine quality control. This subset of PUFs is spiked with dioxin and furan standards and is again subjected to a 16 hour soxhlet extraction. The extract is concentrated down to approximately 1 to 2 ml using a rotary vacuum evaporator (a heated bath approximately 60 degrees centigrade is used during this process). This step is followed by nitrogen blow down of the extract to a final volume of 20 μL . The extract is then analyzed per Quanterra's Standard Operating Procedures (SOP). This Quality Control (QC) procedure is used to determine that the PUFs are indeed free from contamination. If the PUFs pass the QC procedure, the information is documented and filed. All PUFs and filters are subsequently wrapped and stored in individual containers for shipment to the field.

Pre-Spiking Protocol

Ambient air media are prespiked with a single labeled isomer (^{37}Cl -2,3,7,8-TCDD). This spiking scheme is used to monitor sampling efficiency and/or breakthrough during the sampling period.

The spiking solution contains the single labeled isotope in isooctane. The concentration is set at 10 pg/μL and a syringe is used to introduce 200 μL of the solution directly into the PUF media. Precautions are used throughout these processes to eliminate contamination and/or misspike of the PUF prior to shipment to the field.

Blanks

Of the five method blank (MB) samples reported, only one had detectable levels of any congeners and these were, in general, well below the levels seen in the tunnel. The average blank detection limits, presented in Table 3-1, can be used to assess the method detection limits. However, as described later in this section, each sample's detection limits are calculated individually; therefore, those values presented in Table 3-1 may not be exactly those of the tunnel samples. Actual tunnel samples were not blank corrected.

Table 3-1. Summary of average (n=5) blank detection limits in pg/sample.

Congener	pg/sample
TCDDs (total)	3.1E+00
2,3,7,8-TCDD	2.5E+00
PeCDDs (total)	4.5E+00
1,2,3,7,8,-PeCDD	3.9E+00
HxCDDs (total)	3.6E+00
1,2,3,4,7,8-HxCDD	3.7E+00
1,2,3,6,7,8-HxCDD	3.7E+00
1,2,3,7,8,9-HxCDD	3.4E+00
HpCDDs (total)	5.1E+00
1,2,3,4,6,7,8-HpCDD	4.0E+00
OCDD	2.1E+01
TCDFs (total)	2.3E+00
2,3,7,8,-TCDF	2.3E+00
PeCDFs (total)	3.4E+00
1,2,3,7,8,-PeCDF	3.2E+00
2,3,4,7,8-PeCDF	2.7E+00
HxCDFs (total)	2.4E+00
1,2,3,4,7,8-HxCDF	1.3E+00
1,2,3,6,7,8-HxCDF	1.6E+00
2,3,4,6,7,8-HxCDF	1.7E+00
1,2,3,7,8,9-HxCDF	2.1E+00
HpCDFs (total)	3.9E+00
1,2,3,4,6,7,8-HpCDF	2.0E+00
1,2,3,4,7,8,9-HpCDF	3.5E+00
OCDF	5.6E+00

Extraction Protocol

All extraction equipment is washed with a detergent solution, and rinsed with water. This is followed by solvent rinsing with acetone, toluene, hexane and methylene chloride in sequence, to ensure removal of any contamination that might be present.

Extraction glassware is tracked throughout the analytical process and documentation is maintained to verify cleanliness of equipment and to prevent cross contamination of samples.

Field sample PUF and filters are maintained at 4 degrees centigrade until time of extraction. Precleaned apparatus that has gone through a 4 hour cleaning cycle is used for the extraction procedures. Each PUF and associated filter are loaded into the soxhlet body, and the collection vessel is charged with 200-300 ml of toluene.

Quality control is monitored by the addition of a method blank and a laboratory control sample (LCS), that are associated with a specific group of field samples. PUFs that were previously cleaned and passed QC are used as the matrix for the MB and LCS.

A set of nine ^{13}C -labeled standards are introduced into each of the samples including the QC samples. One thousand to 5000 pg per labeled analogue is placed in each sample. In addition, the LCS has a second solution introduced that contains all the 2,3,7,8 substituted target analytes of interest, at a concentration of 200-500 pg/isomer. Whereas the level of internal standards is below that seen in the actual samples, they are used to check the laboratory extraction and cleanup procedures. The LCS sample has spiking concentrations more on the order of the Bore 4 outlet concentrations, but higher than those seen at the inlets or vents.

When spiking is complete, refluxing of solvent through the PUF begins by the application of heating mantles to the collection vessel. The cycling of solvent is allowed to continue for a 16 hour period.

All Fort McHenry Tunnel samples were processed in this manner except for the Bore 4 outlet collocated samples. Each set of collocated samples was extracted together to make one sample. A larger soxhlet body was used and the solvent volume was increased to 600-800 ml of toluene. After concentration these samples were cleaned up as described below with no changes in protocol as a result of the combination of the collocated samples.

At the completion of the extraction cycle the vessel is allowed to cool, the apparatus is disassembled and the collection vessels with the extract are removed for further processing. Each extract is rotary evaporated under vacuum and heat. The extract is concentrated by removing excess solvent. Each extract is then brought up to a volume of 10 ml in toluene, and then split into two 5 ml portions. One portion will continue with clean up steps. The other portion is archived in the event of analytical problems.

A summary of both the internal standards and field surrogate spike-and-recovery data for this project is presented in Table 3-2. These values are for samples that went through the entire extraction and cleanup procedure. In this table the average of 60 experiments is presented along with the standard deviation and the percent relative standard deviation (RSD). Also presented are the highest and lowest recoveries reported for this study. The data show excellent consistency among the 60 recovery experiments conducted. The highest standard deviation was 16%, for both the heptachloro dioxin and heptachloro furan internal standards. It is important to note that the ^{37}Cl -labeled field surrogate showed excellent results with an average 105% recovery and only 7% relative standard deviation. This standard is added prior to the media going to the field and shows that the trapping and recovery of the compounds of interest should be excellent.

Cleanup Procedures

The EPA method allows for a variety of cleanup procedures to be utilized depending on the known or anticipated contaminants and interferences associated with the sample matrix.

All Fort McHenry Tunnel samples were treated with a silica column cleanup, an alumina column cleanup, followed by the carbon-on-silica column cleanup. Acid, base, and neutral silicas and aluminas, as well as carbon-on-silica substrate, are used to eliminate potential contaminants. Interferences such as PAHs, PCBs and others may be present in concentrations far greater than the level of target analytes of interest. These cleanup procedures have all been proven effective in eliminating most interferences and allowing for the collection of the compounds of interest.

After these rigorous cleanup procedures, the sample extract is concentrated down to a 1-2 ml portion by use of a Turbo-Vap. ^{13}C -labeled recovery standard is added and a final volume of 20 μL is achieved by slow evaporation under a dry stream of nitrogen gas in a concentrator. The extract is quantitatively transferred to an injector vial and the extract is ready for analysis.

Table 3-2. Summary of 60 spike and recovery experiments for the Fort McHenry Tunnel Dioxin study.

Internal Standards	Ave	Std Dev	RSD	High	Low
^{13}C -2,3,7,8-TCDF	114	11	10%	133	82
^{13}C -2,3,7,8-TCDD	101	14	14%	120	61
^{13}C -1,2,3,7,8-PeCDF	113	13	11%	134	76
^{13}C -1,2,3,7,8-PeCDD	127	15	12%	170	93
^{13}C -1,2,3,4,7,8-HxCDF	78	8	10%	93	55
^{13}C -1,2,3,4,7,8-HxCDD	87	8	9%	100	59
^{13}C -1,2,3,4,6,7,8-HpCDF	81	13	16%	102	51
^{13}C -1,2,3,4,6,7,8-HpCDD	88	14	16%	110	55
^{13}C -OCDD	76	10	13%	96	46
Field Surrogate					
^{37}Cl -2,3,7,8-TCDD	105	8	7%	129	86

Analysis

Instrumentation required to analyze dioxin and furans at trace levels is very specific with magnetic sector High Resolution Mass Spectrometer (HRMS) being the preferred instrument. Quanterra analyzed the samples using one of three VG-70 SE, and one VG Ultima in the Quanterra HRMS facility. All the instruments are devoted to high resolution dioxin analysis.

Instrument Criteria

The mass spectrometer is operated in the electron ionization mode. A static resolving power of at least 10,000 (10 percent valley definition) must be demonstrated at

appropriate masses before any analysis is performed. Corrective actions are implemented whenever the resolving power does not meet the requirement.

Using a perfluorokerosene (PFK) molecular ion peak, the instrument is tuned to meet minimum required resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) which is the reference signal close to m/z 303.9016 (from TCDF). By using the peak matching unit and the aforementioned PFK reference peak, the exact mass of m/z 380.9760 (PFK) is verified to be within 5 ppm of the required value. Note that the selection of the low- and high-mass ions must be such that they provide the largest voltage differential.

Documentation of the instrument resolving power must then be accomplished by recording the peak profile of the high-mass reference signal (m/z 380.9760) obtained during the above peak matching experiment by using the low-mass PFK ion at m/z 304.9824 as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The format of the peak profile representation must allow manual determination of the resolution, i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The result of the peak width measurement (performed at 5 percent of the maximum, which corresponds to the 10-percent valley definition) must appear on the hard copy and cannot exceed 100 ppm at m/z 380.9760 (or 0.038 amu at that particular mass).

Prior to the initial calibration a Window Defining Mix (WDM) that contains the first and last eluting isomers in each chlorination level is injected into the GC to determine the proper switching times for the SIM descriptors. This solution also includes a Column Performance Solution Mixture (CPSM) used to determine the chromatographic separation between the 2,3,7,8-TCDD and the next closest eluting TCDD isomer. The peaks must be resolved with a valley of $\leq 25\%$.

A five point calibration curve containing all the labeled and unlabeled dioxin and furan isomers is used to calibrate the instrument. Relative response factors (RRF) are calculated for all natives relative to internal standards from a single set of injections. A % RSD for the mean response factors of $\pm 20\%$ for natives and $\pm 30\%$ for internal standards is used to evaluate the curve materials. In addition the signal to noise S/N ratio for GC signals present in every SICP must be ≥ 10 , and the isotopic ratios must be within control limits.

Routine or Continuing Calibration

The mid point of the curve (CC-3) is used as a continuing calibration or daily standard. This standard is run at the beginning of each 12 hour analytical run. The RRF measured for the labeled and the unlabeled standards must be within $\pm 30\%$, and $\pm 20\%$, respectively, of the mean values established in the initial calibration.

All standards are purchased from certified vendors and come with documentation of authenticity. The standards are logged in and assigned an expiration date upon opening. Calibration and spiking solutions are created from these purchased materials, using Quanterra's standard operating procedures for the preparation of standards. Calibration solution concentrations are confirmed using a third party independent solution. When all standard operating conditions are satisfied, analyses are begun.