Mercury Emissions from Motor Vehicles

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The U.S. Environmental Protection Agency initiated a pilot program in 2002 with researchers at the University of Michigan Air Quality Laboratory to investigate motor vehicle mercury emissions. The program included exhaust emissions characterization of vapor and particulate phase mercury from three light-duty gasoline vehicles, one diesel vehicle and mercury analysis of fuel, lubricating oil, engine coolant, brake rotors and brake pads. Mercury was detected in all samples collected. Emission factors for elemental, vapor-phase mercury plus particulate mercury for the light-duty gasoline vehicles ranged from 0.31 to 1.4 ng/mi and for the diesel vehicle from 6.3 to 11.0 ng/mi. Results of the pilot program provide evidence of a mobile source contribution to environmental mercury. The data suggest that some of the factors influencing mercury emissions from mobile sources include oil consumption, driving conditions (including brake wear), and fuel consumption. Limitations of this study include: reactive gas-phase mercury was not measured, vehicles were not tested under cold start conditions, and few vehicles and fuels were tested. In addition, the nationwide fleet is not characterized by the few vehicles studied and emissions from non-road engines have not been measured. Further research is needed in order to estimate mobile source mercury contributions to the national mercury inventory.

Introduction

Interest in the contribution of motor vehicle emissions to environmental mercury concentrations has increased in recent years. Several studies suggest that motor vehicles may be a source of atmospheric mercury. Sediment samples collected in water bodies throughout the United States indicate an association between proximity to vehicular traffic sources and elevated mercury concentrations.[1, 2] Pierson and Brachaczek[3] measured particulate phase mercury collected on Teflon filters in a highway tunnel in the United States using neutron activation analysis. Studies have also reported mercury in crude oil,[4] diesel fuel and gasoline.[5] However, previous motor vehicle emissions tests conducted on chassis dynamometers have found no detectable levels of mercury in vehicle exhaust. These studies relied on x-ray fluorescence of particulate samples to determine mercury concentrations and did not include vapor phase mercury determinations.[6, 7, 8]

The U.S. Environmental Protection Agency (EPA) initiated a pilot program in 2002 with researchers at the University of Michigan Air Quality Laboratory (UMAQL) to investigate mercury emissions from motor vehicles. The aim of the project was to use more sensitive analytical methods to determine if mercury is measurable in motor vehicle exhaust and fuels. Exhaust emissions from gasoline

and diesel vehicles were analyzed for vapor and particulate phase mercury. In order to understand potential sources of mercury in motor vehicle exhaust, fuel, lubricating oil, engine coolant, and brake rotor/brake pad swabs were analyzed for mercury.

Methods

Four, late model (1995 to present), on-road motor vehicles were non-randomly selected for the pilot program. Three light-duty gasoline vehicles (LDGVs) (2001 Ford Crown Victoria, 13,439 miles; 1996 Chrysler Jeep Cherokee, 76,950 miles; 1996 Chevrolet Astro Van, 26,800 miles) and one heavy-duty diesel vehicle (HDDV) (General Motors, 2,538 miles) were evaluated.

Vehicle driving simulation was conducted on a Horiba single 48-inch diameter electric chassis dynamometer. The EPA National Vehicle and Fuel Emissions Laboratory (NVFEL) full-flow, low-particle-loss dilution system provided dilution of vehicle exhaust.[9] A Critical Flow Venturi-Constant Volume Sampler (CFV-CVS) was operated at a nominal flow rate of 750 scfm for flow control of the dilute exhaust. A HEPA filter (99.97% DOP filter efficiency) installed at the dilution air intake removed particles prior to mixing with vehicle exhaust.

All vehicles were conditioned for twenty minutes prior to testing by operation at 50 mph under steady-state conditions. Exhaust samples from the light-duty vehicles were collected for two driving cycles: the Highway Fuel Economy Test (HWFET) and the US06 Supplemental Federal Test Procedure (US06). The HWFET cycle is a chassis dynamometer driving schedule developed by the EPA for the determination of fuel economy for highway vehicles with gross vehicle weight ratings of less than 8500 pounds. The cycle represents near, steady-state highway driving over a 10.26-mile (16.45-km) route. The cycle has an average speed of 48.3 mph (77.7 km/h) and a total duration of 12.75 minutes. The US06 represents aggressive, high speed, and high acceleration driving behavior, rapid speed fluctuations, and typical driving behavior following startup. The cycle is an 8.01-mile (12.8-km) route with an average speed of 48.4-mph (77.9 km/h), a maximum speed of 80.3-mph (129.2 km/h), and a duration of 9.93 minutes. The US06 is used in calculating a composite emissions value in the certification of some model year 2001 and later on-highway motor vehicles. Emissions from the HDDV were tested during the HWFET and the Supplemental Federal Test Procedure Air Conditioning Cycle (SC03). The SC03, like the US06, is used in calculating a composite emissions value in the certification of some model year 2001 and later on-highway motor vehicles. The SC03 cycle is a 3.6-mile (5.8-km) route with an average speed of 21.6-mph (34.8 km/h). The SC03 includes less aggressive driving than the US06 and was determined to be more suitable for the diesel vehicle used in this pilot program.

Prior to each composite test, the exhaust transfer line, dilution tunnel and all sample lines were conditioned for twenty minutes. Samples were collected over three continuous test cycles for each vehicle and driving cycle combination. This sampling schedule provided two sets of samples for each of the four vehicles tested. In addition, swab samples were collected from the brake pads and rotors of each vehicle.

All sampling equipment, including Teflon filter packs, forceps and Petri dishes, was acid cleaned prior to use in sampling. Fine particulate mercury samples were collected at a flow rate of 16.7-L min^{-1} onto 47-mm quartz filters (Pallfelx, Gelman Sciences) that were pre-baked at 500C for one hour to reduce background levels of mercury.[10] Semi-continuous gaseous elemental mercury measurements were measured using a Tekran (Model No.2537A) during all tunnel conditioning, vehicle conditioning, and vehicle testing operations. Integrated gaseous elemental mercury samples were collected on gold-coated sand traps. Vapor and particulate phase mercury measurements for the dilution air were collected through a port located after the HEPA filter and before the introduction of vehicle exhaust.

All mercury samples were analyzed using cold vapor atomic fluorescence (CVAFS). Particulate mercury and brake pad/rotor swabs were acid-digested and analyzed in a Class 100 clean room. A detailed description of the preparation and analysis procedures used can be found in Keeler et al.[11] For each vehicle tested, fuel, lubricating oil and engine coolant samples were collected after operation on the dynamometer. Fuel and coolant samples were taken directly from the vehicle reservoirs. Lubricating oil samples were obtained from the inside of the vehicle's oil filter. Liquid and swab samples were digested with bromine monochloride and analyzed using CVAFS.

Total hydrocarbon (THC), CO, NO_x, and CO_2 concentrations were measured in the dilution air and diluted vehicle exhaust to serve as reference measures for background air concentrations and vehicle operating conditions. Ambient temperature, relative humidity and atmospheric pressure were measured electronically during the tests. Vehicle speed was measured using a digital optical encoder as part of the driver's aid system.

Results

Table 1 lists mercury emission rates obtained during the pilot program. The rates shown include vapor-phase elemental mercury and particulate mercury. Emission rates ranged from 0.3-0.5 ng/mi for LDGVs on the HWFET test and from 1.2-1.4 ng/mi for the same vehicles tested on the US06 driving schedule. The HDDV emission rates ranged from 6.4 on the SC03 test to 11.1 on the HWFET test.

Table 1. Emission rates for vapor phase elemental plus particulate mercury

Test Vehicle/Driving Cycle	Number of Tests	Emission Rates (ng/mi)
Light-duty gasoline vehicles/HWFET tests	3	0.3-0.5
Light-duty gasoline vehicles/US06 tests	2	1.2-1.4
Heavy-duty diesel vehicle/HWFET test	1	11.1
Heavy-duty diesel vehicle/SC03 test	1	6.4

Mercury was detected in all motor vehicle fluids sampled (Table 2). Among the fluid samples collected from the LDGVs, lubricating oil contained the highest concentrations of mercury, ranging from

239-578 ng/L (n=4). The engine coolant samples from the LDGVs contained the lowest levels of mercury among the fluids tested in this pilot program, with concentrations ranging from 0.2-2.5 ng/L (n=4). Three gasoline samples were analyzed and mercury concentrations in these samples ranged from 52-189 ng/L. The mercury content of these gasoline samples was substantially higher than the 4.2 ng/L mercury concentration in the diesel fuel sample.

Table 2. Mercury content in vehicle fluids (number of samples)

Fluid Type	LDGV Fluid Concentrations (ng/L) (n)	HDDV Fluid Concentrations (ng/L)
Fuel	52-189 (3)	4.2 (1)
Lubricating Oil	239-578 (4)	15 (1)
Engine Coolant	0.2-2.5 (4)	6.9 (1)

During a portion of one US06 LDGV test, the computer system controlling the dynamometer braking assist system failed and the vehicle operator was required to brake heavily. During this event, gaseous mercury levels in the dilution air increased by a factor of fifty. This test was omitted from the composite results of emission factors reported in Table 1, but inspired the collection of swab samples from brake rotor/brake pads of each vehicle for mercury analysis. Swab samples were collected from the front and rear brake rotors and pads of the three LDGVs and both front and rear brake rotor/pads of the HDDV. Mercury was detected in all brake swab samples.

Discussion

The mercury emission factors measured as part of this NVFEL pilot study are substantially lower than the emission factor reported by Pierson and Brachaczek (1983) of 2.09 µg/mi. This finding is consistent with mercury analysis in other matrices conducted in the 1980's in the absence of clean techniques (e.g., pre-firing filters to consistently lower blank levels, acid-cleaning of filter holders and sample vials, use of ultrapure chemicals for extraction, etc.). In addition to the absence of clean techniques, an important factor likely to have contributed to the elevated particulate mercury emission rate reported by Pierson and Brachaczek is resuspended dust in the tunnel in which sampling was conducted. There are also significant differences in fuel formulations in the 1980's and current fuels, as well as engine technologies that could influence exhaust concentrations of mercury and the gas-particle partitioning of mercury in the exhaust.

LDGV mercury emissions over the US06 driving schedule were two to five times higher than over the HWFET driving schedule. These data indicate the importance of different driving conditions and behaviors on mercury emissions. Increased braking and hard accelerations are likely to increase mercury emissions from brake wear as well as increased fuel consumption and potentially oil

consumption. The potential role of tire wear on mercury emissions has not been evaluated but could also contribute. The HDDV mercury emissions were higher over the HWFET test than the SC03 test. This is potentially due to the difference in fuel and oil consumption over the 10.26 mile HWFET test compared with the 3.6 mile SC03 test.

The exploratory nature of the NVFEL pilot program provided limited fuels analysis, and yet, these data suggest that the mercury concentration in fuel range widely. The only other study of which we are aware, using methods capable of quantifying trace mercury levels in motor vehicle fuels was a report by Liang et al.[12] These authors used methods similar to those reported here (bromine monochloride extraction followed by CVAFS) to analyze gasoline, kerosene, diesel, and heating oil samples. Of the five gasoline samples from the U.S. reported by Liang et al., mercury concentrations ranged from 0.22–1.43 ng/g and the one U.S. diesel fuel sample had a mercury concentration of 0.40 ng/g. To compare these results to those reported in this study, the units were converted to mass per volume by multiplying by the density of gasoline (734.4 g/L) and diesel (847.2 g/L). The resulting concentrations of mercury in gasoline are 162-1,050 ng/L and in diesel the concentration is 339 ng/L. The concentration of mercury in gasoline reported by Liang et al. overlap with the gasoline mercury concentrations reported here, but the upper end of the range is an order of magnitude higher than in the NFVEL pilot study. The concentration of mercury in the diesel sample reported by Liang et al. is two orders of magnitude higher than the diesel sample from the NVFEL pilot study.

The wide variation in mercury content of fuels is likely to be influenced by the mercury concentration in the crude oil as well as many other factors including fuel conditioners, lubricity additives, fuel-borne catalysts and other additives. Wilhelm[13] summarized the literature for mercury concentrations in crude oil, reporting values that range over three orders of magnitude. We are not aware of any reports of mercury analysis of fuel additives in which the appropriate methods capable of quantifying trace levels of mercury have been employed. A comprehensive survey of mercury concentrations in fuel would be required to estimate the possible range of mercury available for emission from the various types of fuels.

Conclusions

Results of this pilot NVFEL program provide evidence that gasoline and diesel motor vehicles contribute to environmental mercury. Tailpipe exhaust measurements indicate that mercury emissions vary depending on driving conditions and fuel use. This pilot study identified brake wear as a potentially significant source of mercury emissions from mobile sources. However, a quantitative evaluation of mercury emissions from brake wear was beyond the scope of this study. Motor vehicle sources of mercury include, but are not limited to the fuel, lubricating oil and brake wear. Tire wear is a potential source of mobile source mercury not yet investigated.

Although these pilot data indicate that the mercury emission factors may be low, extreme care must be exercised in applying these data nationally. This study only evaluated three light-duty gasoline vehicles and one heavy-duty diesel engine. The representativeness of these vehicles to the national fleet

cannot be determined. All vehicles tested were procured from the same region of the country and tested using "in-use" fuel and oil, so variability in the mercury content of the fuel is not likely to have been represented. Perhaps, most significantly, vehicles were not tested under cold start conditions. For a number of compounds, including particulate matter and benzene, cold start emissions account for a majority of the total emissions.

Divalent, gas-phase mercury emissions, which may account for a significant fraction of total mercury emissions from mobile sources, were not quantitatively measured in this study. Understanding the divalent mercury component of mobile source emissions is particularly important due to the rapid deposition rate and potential for rapid methylation in waterways.

Emissions were only analyzed for on-road vehicles, so a large category of mobile sources, specifically non-road engines and fuels, were not characterized as part of this work. These study limitations should be addressed before attempting to estimate the national contribution of mobile sources to mercury emissions.

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Keywords

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