HEI

STATEMENT

Synopsis of Research Report 133

HEALTH EFFECTS INSTITUTE

Characterization of Metals Emitted from Motor Vehicles

BACKGROUND

Metals comprise a complex group of elements with a broad range of toxicity, including effects on genes, nervous and immune systems, and the induction of cancer. Some metals are toxic at very low levels; others are essential to living systems at low concentrations, but may be toxic at higher concentrations. Metals may exist in several valence states that differ in toxicity and may be associated with organic matter and inorganic materials that can affect their toxicity. The presence of metals in the environment has received a great deal of attention in recent years. Their accumulation in the environment is of concern because of their persistence. Some scientists believe that transition metals are particularly toxic components of particulate matter (PM).

In 1998, HEI issued Request for Preliminary Applications 98-4, *Research on Metals Emitted by Motor Vehicles*. The goal of the RFA was a broad investigation of metals that may be found in automobile emissions, in particular those found in tailpipe exhaust. Metallic components of fuel additives were a high priority, but metals found in other emissions (such as those derived from fuel lubricant, engine wear, catalytic converter, or brake pads) were also of interest.

APPROACH

Dr Schauer collected and characterized metals in fine and coarse particles from a variety of sources associated with on-road motor vehicles in summer and winter, including tailpipe emissions (from both gasoline and diesel vehicles), dust from brake wear and tire wear, roadway dust, and roadway dust containing salt applied to roadways in winter. In addition, total roadway emissions were measured in two roadway tunnels. Metals were also characterized in ambient air from three urban sites. Use of sensitive analytic techniques such as inductively coupled plasma mass spectrometry (ICP-MS) allowed measurement of a variety of elements in these emissions and subsequent development of profiles for each source. These profiles were compared to the profiles developed for the roadway tunnels by using a chemical mass balance (CMB) model, in order to determine the relative contribution of various sources to total roadway emissions. Iterated confirmatory factor analysis (ICFA) was used to determine the relative contribution of various sources to ambient particulate matter collected at the three ambient locations. To preliminarily address bioavailability of metals, ambient and tunnel samples were examined in a study that determined solubility in a synthetic fluid that was designed to mimic human epithelial lung lining fluid to better estimate the biologically available pool of metals in particulate matter.

Dr Schauer's study evaluated the use of tunnels for identifying the source contributions of metals from a variety of different types of automobile emissions. The study objectives address the use of improved methods for measuring many metals that occur at low levels and application of these methods to tunnels, automobile-associated emissions, and ambient air. Measurements from tunnels were thought to be useful for evaluating exposures to emissions from in-use vehicles. He used the two newer methods, ICP-MS and ICFA, along with more conventional analytic techniques such as x-ray fluorescence spectrometry (XRF) and CMB models, to identify source profiles for various components of mobile source emissions.

RESULTS

The combined use of ICP-MS and XRF allowed detection of 43 elements. The concentrations of 12 elements (aluminum, silicon, phosphorus, sulfur, potassium, calcium, scandium, germanium, selenium, bromine, iodine, and cerium) were determined by XRF elemental analysis. The application of ICP-MS allowed measurement of concentrations of 31 additional elements. Use of ICP-MS, with its greater sensitivity for metals, allowed the detailed

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This Statement, prepared by the Health Effects Institute, summarizes a research project funded by HEI and conducted by Dr James J Schauer, Environmental Chemistry and Technology Program and Wisconsin State Laboratory of Hygiene, University of Wisconsin, Madison WI. The complete report, *Characterization of Metals Emitted from Motor Vehicles*, can be obtained from HEI or our website (see reverse side).

profiling of elements that was necessary for the subsequent identification of profiles that can be used for assessing the contribution of different sources to metal levels in the tunnel.

Using a CMB model, the investigators compared source profiles for total roadway emissions, as measured in tunnels, to profiles for the individual emissions sources (resuspended road dust, brake dust, tire dust, and tailpipe emissions from gasoline- and diesel-powered vehicles). Using these source profiles, and excluding results from light weekend traffic in summer in one tunnel, CMB modeling predicted 63% to 160% of the total PM mass in the tunnels. Measured emission rates and values calculated using CMB modeling added further support for the modeling results.

ICFA combines elements of confirmatory and exploratory factor analysis in a way that makes use of knowledge of some source profiles while generating updated profiles for sources that are less well defined. Results of this analysis indicated that the two organic source profiles were dominant contributors of ambient PM_{10} and that the road salt profile was a dominant contributor to ambient chloride. Not surprisingly, organic and elemental carbon dominated the results of the analysis; however, by removing these values from the model, the investigators were able to perform a source attribution for metals. They concluded that organic sources were major contributors for 14 species in ambient PM_{10}: organic carbon, elemental carbon, magnesium, aluminum, potassium, calcium, iron, vanadium, manganese, arsenic, strontium, cadmium, barium, and cerium. Road salt was found to be a major contributor of chloride and sodium.

The solubility tests used samples from ambient air and from tunnels in a synthetic lung fluid. The results indicated that many elements could be leached into the fluid. The investigators found eight transition metals (silver, titanium, iron, tungsten, copper, zinc, manganese, and cadmium) from tunnel samples, and eight (titanium, tungsten, copper, zinc, manganese, chromium, vanadium, and molybdenum) from ambient samples, in the leachate, with a high solubility observed for several elements.

SUMMARY AND CONCLUSIONS

This was a valuable study, performed by an investigator team with expertise in measuring trace levels of metals in environmental samples. The methods they used to approach the study problem were excellent, and the study generated solid information that could be important for a range of activities, including emissions inventories. The team took a multidisciplinary approach to the examination of metals from mobile sources (including vehicle sources besides the tailpipe), weaving together biology, chemistry, and source apportionment techniques. An important aim of this study, to measure exposure in people conducting activities near traffic, was not addressed, however, the results from the other aims are valuable individually, and even more valuable when examined together.

Although this study provides a large amount of useful information, several limitations should be noted before more general conclusions are drawn: (1) Care should be taken if extending the roadway emissions results from this study in these specific locations more broadly. (2) Similar care should be taken in extending the ambient air sampling and subsequent source apportionment results. (3) ICFA needs to be validated through replication in other studies, including studies in different environments and with different compositions of vehicles, and evaluated against other methods. (4) The data generated from this study should be considered exploratory in nature, providing new information for and insight into the application of techniques to studies of air pollution related to mobile sources.

The study provides useful data, especially with respect to exposure from all types of mobile sources (not just tailpipes). The study by Schauer and colleagues brings a novel approach, ICP-MS, to the characterization of metals in PM, which has been a problem because measurement of trace elements has heretofore been hindered by limits of detection. This technique lowers the detection limits significantly, making measurement of trace metals possible. The application of another new technique, ICFA, allows these measurements to be used in subsequent source apportionment. This research also involved using synthetic fluid to determine the fraction of metals that is soluble in a biological environment and thus may interact with cellular components. This study, with its multidisciplinary approach, provides important tools and presents a useful approach for gathering information about which metals (and sources of these metals) are linked with pathology of the respiratory systems in asthma and other diseases.

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