PAST AND PRESENT CONTRIBUTION OF LEADED GASOLINE COMBUSTION TO THE GLOBAL DIOXIN BUDGET

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Introduction

Approximately ten studies have been performed to measure dioxin emissions from motor vehicles burning leaded gasoline. Due to the differences in vehicle types used, fuel compositions (especially scavenger types and concentrations), sampling methodologies (i.e. tailpipe vs. tunnel), and analyses (types of PCDD/F, PBDD/F, or PHDD/F looked for and differences in analytical techniques), there is significant uncertainty in the emission factors derived for leaded gasoline powered vehicles[1,2,3,4,5,6,7]. Although leaded gasoline sales currently account for approximately 21% of global gasoline sales, lead was heavily utilized as an anti-knock additive until the late 1990s[8]. Because long-range transport and distribution of fine particles is possible and some PHDD/F have long residence times in the environment and in fatty tissues, we hypothesize that vehicles burning leaded gasoline may have contributed significantly to the global dioxin budget in the past and possibly continue to do so in the present. By analyzing archived hi-vol air filters (1974-1980), collected from an area in California that has had few to no major dioxin sources historically, we hope to provide evidence for the hypothesis that automobiles fueled with leaded gasoline have been significant, yet underestimated sources of global dioxin and continue to be so in some countries.

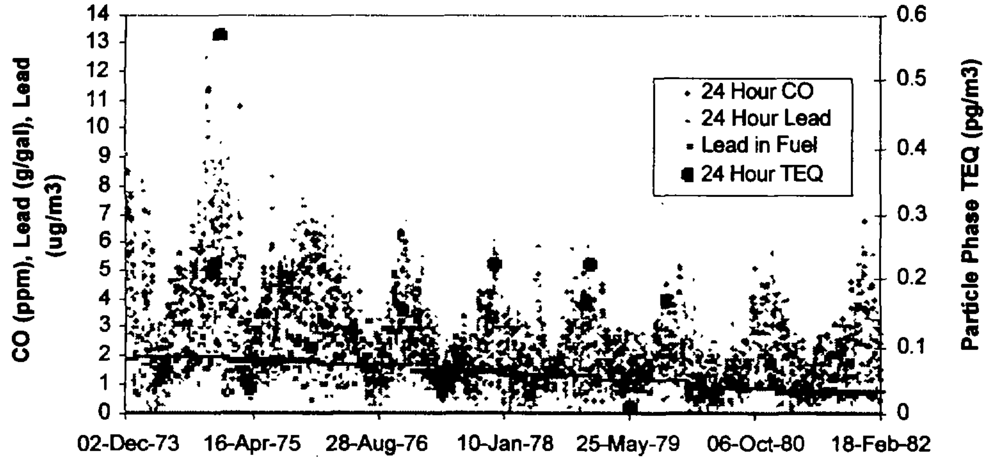
Methods and Materials

Seventeen archived hi-vol air filters (including one cellulose blank and one glass fiber blank) from the Magnolia air-monitoring station (Riverside, CA) were sent to the Ontario Ministry of the Environment for PCDD/F analyses. Portions of these filters had also been previously analyzed for lead (Pb) as part of routine air monitoring studies prior to being archived. For the PCDD/F analyses extraction, removal of interferences and detection by gas chromatography/high resolution mass spectrometry were performed according to MOE method E3319 (equivalent to EPA Method 1613). Samples were extracted by Soxhlet apparatus following addition of ^{13}C-labeled dioxins and furans. Sample extracts were cleaned using a three-stage (acid/base silica, alumina and activated carbon) cleanup procedure. Cleaned extracts were analyzed by gas chromatography/isotope dilution high resolution mass spectrometry (GC/HRMS). Chromatographic separations were achieved on a 60M DB-5 0.25mm, 0.25um column using helium as carrier gas. Splitless injection was used. The temperature program was: 100°C for 1 min; 30°/min to 200°C, 3°C/min to 235°C, hold for 10 min, 6°C/min to 300°C hold for 15 min. HRMS analysis was carried out on a VG Autospec mass spectrometer tuned to 10,000 resolving power (10% valley) in the selected ion monitoring mode.

Results and Discussion

The "Magnolia" samples were analyzed for PCDD/F and compared with the previously measured values for CO and Pb on the same sampling days. A fairly strong correlation was found to exist between particle phase toxic equivalency (TEQ) and carbon monoxide (CO) for the years 1973-1980 (Ú = 0.82, Figure 1).

Figure 1: Ambient TEQ, CO, Pb, and Lead In Fuel
Magnolia Station, Riverside



The correlation between TEQ and ambient lead (Pb) for the years 1973-1980 is lower, Ú = 0.56, and the correlation between TEQ and total suspended particulate (TSP) for the same time period is Ú = 0.73. The correlation between CO andPb for the years 1973-1980 is Ú = 0.57, that for CO and TSP is Ú = 0.29, and that forPb and TSP is Ú = 0.35.

Motor vehicles are the primary sources of CO in the South Coast Air Basin (in which the city of Riverside is located). The ARB estimates that over 90% of 1996 CO emissions in Riverside are due to vehicular sources[9]. Approximately 60% of TSP emissions in the South Coast originate from "road dust"[9]. The Magnolia station was chosen as the source of the archived filters because 1) it is often down-wind of the Los Angeles area, 2) it has a long history of continuous operation, 3) it is not near any known point sources of dioxin, 4) it is a "neighborhood-scale" air monitoring station meaning that it samples air representative of a spatial scale of a half kilometer or more. Because selected samples from the Magnolia station were analyzed, those drawn during high and low ambient Pb levels, several sampling periods occurred during periods of high CO as well, corresponding to low wind speed, stable atmospheric conditions. We believe the samples primarily represent local emissions during those periods of poor ventilation with some relatively smaller contributions of upwind "background" air. The correlation between ambient TEQ and CO is fairly strong and combustion sources in the local area are primarily vehicular, supporting the hypothesis that vehicles are responsible for the observed TEQ levels in the Riverside area. From past studies, it is known that a significant portion of the mass of Pb-particles are deposited close to the roadway, perhaps accounting for the lower correlation with exhaust particles. The somewhat lower correlation of TEQ with Pb and TSP than with CO, which would track fine particle emissions better, is understandable. Chlorinated dioxin formation is typically related to both the carbonaceous content of the particles as well as the presence of chlorine, and to a lesser extent the actual chlorine concentration in the fuel as determined from studies of waste combustion[10].

TCDF contributed significantly to total TEQ before the phase-out of leaded gasoline began (Figure 2). In their second vehicular study, Marklund *et al.* found that the less chlorinated PCDD/F homologues, most notably TCDF, predominated in the leaded fuel combustion emissions profile[5]. Phaseout of leaded gasoline as well as the introduction of catalytic converters into the vehicle fleet may have been responsible for the observed decreases in TCDF from 1974-1980.

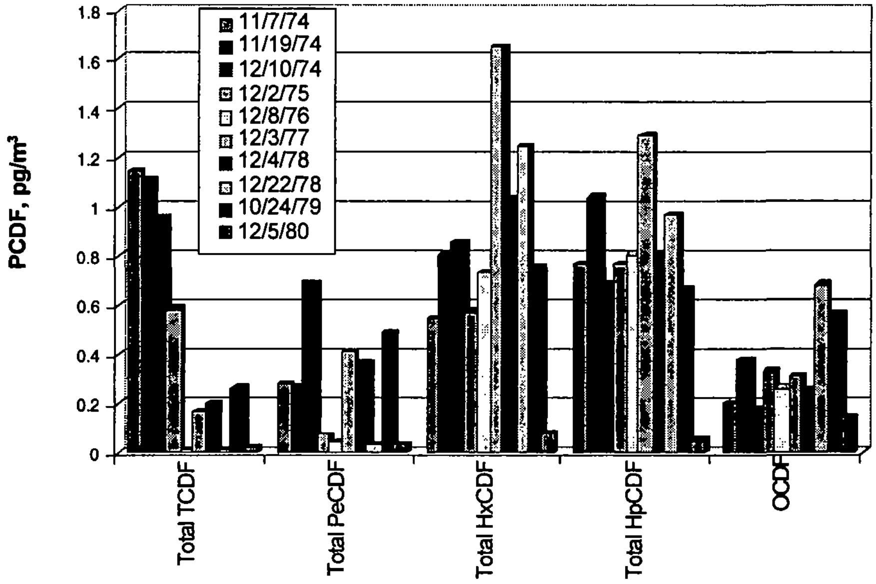


Figure 2: Winter Furan Homologue Profiles for Riverside Filters

Results of vehicular emissions testing by Haglund *et al.* and Schwind *et al.* indicated that large amounts of brominated or mixed halogen dioxin form during leaded gasoline combustion with chlorinated and brominated scavengers present[2,5]. PBDD/F and PHDD/F analyses are not generally performed as some PBDD/F and PHDD/F are unstable in the environment, there are no established TEFs for the various toxic isomers, detection is arduous, and only a few standards are commercially available[11]. Our future work will focus on detection of PHDD/F in our previously extracted filters and simulating environmental conditions in the laboratory that might allow Br-Cl exchange reactions to occur, thereby increasing the concentrations of PCDD/F in the environment after initial emissions of PHDD/F.

If vehicles burning leaded gasoline have been and continue to be significant sources of PCDD/F globally, widespread distribution in the environment and the drop in PCDD/F levels during and after leaded gasoline phaseout in many parts of the world may be better explained.

Acknowledgments

The authors wish to thank Debbie Niemeier of UCD, Sue Twiss (formerly of AIHL), Richard Schneider of SCAQMD, Dennis Goodenow of CARB, Bruce Selik of SCAQMD, Pamela Brodowicz of EPA, Dwight ODA of CARB, and the many other people from CARB, SCAQMD, EPA, and NCDC who have helped us with data collection and analysis.

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