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Toxic Air Contaminants Monitoring

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The California Air Resources Board is required by State law to identify and control toxic air contaminants (TAC). In 1985, the ARB established a twenty station toxic monitoring network within major urban areas to provide data to determine the average annual concentrations of toxic air contaminants as input to the identification process, and to assess the effectiveness of controls. The ARB's toxic air contaminant monitoring programs are described below.

Volatile Organic Compounds - VOCs are organic compounds that can vaporize easily at ambient temperatures. Some VOCs are highly reactive and play a critical role in the formation of ozone. Other VOCs have adverse, chronic, and acute health effects. In some cases, VOCs can be both highly reactive and potentially toxic. Sources of VOCs include motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations.

Carbonyl Compounds - Carbonyl compounds (aldehydes and ketones) contain a carbon atom and an oxygen atom linked with a double bond (C=O). Some carbonyls are highly reactive and play a critical role in the formation of ozone. Other carbonyls have adverse chronic and acute health effects. In some cases, carbonyls can be both highly reactive and potentially toxic. The major sources of directly emitted carbonyls are fuel combustion, mobile sources, and process emissions from oil refineries. To date, the ARB monitors three carbonyls: formaldehyde, acetaldehyde, and methyl ethylketone (MEK).

Toxic Metals - The measurement of ambient arsenic, cadmium, chromium, manganese, nickel, lead, copper, zinc, sulfur, titanium, vanadium, iron, cobalt, selenium, strontium, zirconium, molybdenum, palladium, tin, antimony, and platinum is done in support of California's Toxic Air Contaminant Identification and Control Program. This program that began in 1983, is designed to identify and then control chemical, physical or biological agents that are found in ambient air and that interfere with life processes. Analysis is done by inductively coupled plasma - mass spectrometry.

Hexavalent Chromium - The hexavalent chromium (chromium VI) monitoring program is conducted in support of California's Toxic Air Contaminant Identification and Control Program. Chromium compounds exist in several different chemical (oxidation) states, but only two of them, trivalent chromium and hexavalent chromium, are commercially or environmentally important. Hexavalent chromium was identified as a TAC by the Board in January 1986. In California, the primary sources of hexavalent chromium are chrome plating operations and as a corrosion inhibitor in cooling towers. Hexavalent chromium is analyzed by ion chromatography.

Sampling/Monitoring

Monitoring Activities summarizes the network and the monitoring methods for halocarbon and aromatic hydrocarbons, carbonyls, polynucleararomatic hydrocarbons, and toxic metals. It includes sampling schedules, number of sites operating in the State, methodology used by the ARB, U.S. EPA reference method, and data availability.

Monitoring Schedule for Twelve-Day Sampling

The Toxic programs use the one-in-twelve sampling schedule derived from U.S. EPA's monitoring sampling schedule calendar.

Laboratory Analysis

Laboratory analyses of all the ambient air samples are conducted using state-of-the-art techniques. VOC and oxygenated compound samples are collected in stainless steel canisters and are analyzed in the laboratory by gas chromatography - mass spectrometry (GC-MS) methods for butadiene, aromatic and halogenated, and oxygenated hydrocarbons. Carbonyl compounds in ambient air samples are collected into adsorbent cartridges and analyzed by high performance liquid chromatography (HPLC). Metals are determined by inductively coupled plasma - mass spectrometry (ICP-MS), and hexavalent chromium by ion chromatography (IC).

Laboratory Standard Operating Procedures

Each method used to generate laboratory data has a written standard operating procedure (SOP). These procedures are followed each time the method is used to produce data for record. The following is a list of the laboratory SOPs currently used in the analysis of toxic air contaminants.

Organic Compound Analyses

- **SOP MLD022** - Determination of Carbonyl Compounds in Ambient Air Using High Performance Liquid Chromatography.
- **SOP MLD058** - Determination of Aromatic and Halogenated Compounds in Ambient Air by Gas Chromatography / Mass Spectrometry.
- **SOP MLD066** - Determination of Oxygenates and Nitriles in Ambient Air by Capillary Column Gas Chromatography / Mass Spectrometry.

Inorganic Compound Analyses

- **SOP MLD061** - Trace Elemental Analysis of Ambient Air Particulate Samples Using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
- **SOP MLD039** - Extraction and Analysis of Hexavalent Chromium by IC.

Quality Assurance

The Quality Assurance Section conducts laboratory performance audits to ensure the accuracy of the toxic air contaminant data generated by ARB's monitoring program. The performance audit includes both laboratory and field assessment elements.

Publications and Downloadable Files

Report on a Parallel Carbonyl Monitoring Study Using C18 and Silica Gel Sampling Media, Gabriel Ruiz, Monitoring and Laboratory Division, January 20, 1998. (*Acrobat, 129 KB*)

Abstract:

In 1996, the California Air Resources Board conducted a one-year study to identify and evaluate possible bias between two sampling media for ambient carbonyl pollutants. Parallel samples were collected on silica gel and C18-bonded silica gel (C18) cartridge sat each of two sites, at a flow rate of 0.7 liters per minute over a 24-hour period every 12 days.

The results of the study show a negative bias in the sampling efficiency of the C18 media when compared to silica gel, especially at higher ambient carbonyl concentrations. Breakthrough was a widespread problem and one of the causes for the poor collection efficiency of the C18 sampling media. The silica gel sampling media demonstrated superior properties in terms of precision and resistance to breakthrough under the program's sampling conditions.

Study to Determine the Effect of Moisture on Volatile Organic Compound Recovery Rates for Thru-The-Probe Audits into Stainless Steel Canisters, Alice Westerinen and Barry B. Reisman. Technical paper presented at the U.S.EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina, May 7-9, 1996.

Abstract

Through-the-Probe (TTP) audits of criteria pollutants have been a part of the California Air Resources Board's (ARB) quality assurance program since 1982. The TTP audit allows us to check the integrity of the entire sampling and analysis phases of ambient air pollution monitoring. By auditing thru-the-probe we can detect not only problems associated with instrument calibration and operation, but also problems associated with the station probe line from leaks or contamination. In 1989 we expanded the TTP audit program to include the ambient toxic monitoring program. This field audit program joined an existing laboratory audit program for volatile organic compounds (VOCs). Using this approach we were able to determine the field and lab biases and identify areas for improvement in the network. Based on the TTP audits, the ARB conducted a two part canister comparison study to determine the effect of canister moisture on VOC recovery rates from stainless steel canisters. The results of the study will be used to determine the best auditing method for VOC recovery. In Part 1 of the study, we compared the results of standard gas administered into dry canisters with the results of wet injected canisters. The results confirmed improved sample recovery utilizing wet injected canisters for VOC sampling. Humidifying the sample canisters with high grade water improved recovery rates in eight out of 18 VOCs while using a pre-run zero air purge. In Part 2 of the study, wet injected canisters were compared with canisters humidified by adding moisture to the diluent zero air stream. Both audit procedures used a pre-run zero air purge. The humidified diluent ensured all components of the collection system were exposed to moisture prior to being combined with the audit gas and administered to the probe. This practice improved VOC recovery rates over the wet injected canister method in three out of 18 VOCs. This paper is a report on the results of the two part canister humidification study.

Ambient Trends of Benzene in California from 1990 through 1995, Donald Hammond. Technical paper presented at The U.S. EPA /AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina, May 7-9, 1996. (*HTML version*) (*Acrobat, 38KB*)

Abstract

The California Air Resources Board has for the past six years maintained a routine, canister-based ambient toxics monitoring network in urban areas of California. The ambient record is now extensive enough to evaluate the trend of toxic pollutants within the State. This paper evaluates the trend in benzene at seventeen different sites in major population centers in California between 1990 and 1995. Even when considering measurement variability, a significant downward trend in ambient benzene concentrations has been observed throughout the State with an average reduction of 49 percent during the study period. The paper also presents emissions inventory trends of benzene for the same period whose reduction can be attributed to the vehicle emission controls and clean fuel programs.

Voyager Data Files

- Toxics Program Data - PKWare zipped file containing preliminary data for Toxic pollutants sampled at 26 sites from January 1, 1990 to October 30, 1994. Some of these sites do not have toxic data for the entire period. The TOX_AVG.VOY database file contains quarterly and annual averages for most of the toxic compounds found in the TOXIC.VOY file. The Voyager files were used as a quality assurance tool to review the data generated. (toxicvoy.zip, 246K)

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