

Air Toxics: Sources and Monitoring in Texas

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Since the late 1980s, federal legislation has required industries to publicly report their annual emissions of toxic compounds. Industry reports show the largest contributor to toxic emission levels in Texas is the massive concentration of petrochemical industries along the Gulf Coast. It is interesting to note that although Texas produces over 50% of the nation's synthetic chemicals, it discharges less than 8% of the nation's toxic emissions. However, in response to growing concerns about the effects of these toxic emissions, the Texas Natural Resource Conservation Commission (TNRCC) initiated a long-term program for monitoring toxic chemicals in the air. This article provides details of this monitoring program as well as industry-funded toxic monitoring networks in Texas. This includes information on the technology currently being used for sample collection and analysis as well as plans for implementing methods that are on the technological horizon. Finally, details of some key measurements from the state's air toxics monitoring network will be provided along with an explanation of how they impact current air quality trends in Texas. — *Environ Health Perspect* 103(Suppl 6):223–228 (1995)

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Introduction

Policy-relevant air quality research and measurements have been the basis for air quality management and regulatory decisions in the United States for the past 25 years. The Federal Clean Air Act of 1970 established a regulatory process requiring that state governments take the lead in air quality management decisions. The Federal Clean Air Act Amendments of 1990 expanded this responsibility in a comprehensive set of requirements that is fundamentally changing the process by which clean air is achieved. Never has the need for good science based on rigorous measurements been greater.

Texas has developed a comprehensive strategy for ambient air quality and source-oriented monitoring designed to position the state as a national leader in the application of scientific measurements in the development of sound environmental policy. Many health concerns drive the need for monitoring. Some concerns are national in scope, particularly as they relate to pollutants for which the U.S. Environmental Protection Agency (U.S. EPA) has established National Ambient Air Quality Standards (NAAQS). These designated criteria pollutants include ozone, sulfur dioxide, nitrogen dioxide, carbon

monoxide, lead, and particulate matter less than 10 microns in diameter (PM_{10}). Human health effects of air pollution associated with these pollutants are continuing to be documented through multidisciplinary approaches (1). Some of these pollutants have been associated with the incidence and prevalence of asthma, which is the topic of this workshop. Other pollutants that do not currently have national standards but which have been generally identified in the Federal Clean Air Act Amendments as air toxics are also under discussion as possibly being associated with asthma.

This article will provide a brief description of air toxics emissions in Texas, describe current monitoring strategies in Texas, provide information on data available for analysis, include information on some air quality trends in the state, and project future monitoring activities and technology for the state.

Air Toxics Emissions in Texas

The 1990 Amendments to the Federal Clean Air Act fundamentally changed a previously cumbersome process of listing and regulating hazardous air pollutants (HAPs) by revising Section 112 with provisions that:

- explicitly list 189 HAPs that require regulation
- require technology-based standards for reducing emissions
- require risk-based controls after evaluating residual risk remaining after implementing technology-based standards
- establish an accidental release program.

Texas ranks first nationally in emissions of air toxics, with 157.5 million

pounds reported to the U.S. EPA from Texas industries in 1992 (2). It is important to note, however, that while Texas produces over 50% of the nation's synthetic chemicals, it discharges less than 8% of the nation's toxic emissions (3). U.S. EPA's Toxics Release Inventory (TRI) indicates air toxic emissions have declined by 20% between 1987 and 1991. This downward trend can be attributed to a number of factors including clarification of reporting requirements, real reductions in emissions required by existing regulations, and voluntary reductions perhaps associated with the Texas Natural Resource Conservation Commission (TNRCC) Clean Texas 2000 Program.

Current Monitoring Strategies in Texas

Source Monitoring

Direct measurement of industrial emissions from stacks, flues, and other emission points has been a cornerstone of air pollution regulation for the past 20 years. Federal emissions standards for particular processes covered by federal New Source Performance Standards (NSPS) and National Emissions Standards for Hazardous Air Pollutants (NESHAP) have long required that companies measure actual emission levels. Since the largest concentrations of air contaminants occur downwind of sources, the TNRCC has developed an extensive source-oriented monitoring strategy. The backbone of the source-oriented monitoring strategy is the agency's mobile monitoring operation. The mobile monitoring operation includes a self-contained mobile laboratory for on-site

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analysis, three specially equipped sampling vans, and an air toxics response trailer. These mobile sampling platforms allow for intensive source-oriented monitoring projects that capture maximum exposure conditions downwind of industrial facilities. Monitoring techniques used include real-time gas chromatography and sorbent tube sampling with subsequent gas chromatographic and ion trap analysis. In addition, when determined appropriate, source-oriented special purpose semipermanent, fixed monitoring sites are established to gather data on particular sources.

Ambient Air Monitoring Networks

Although Texas conducted its first air study as early as 1952 and deployed particulate samplers in 1961, extensive air quality monitoring did not begin until 1971, as required by the 1970 Federal Clean Air Act Amendments. By the mid-1970s, most of the state's networks were in place to monitor for the U.S. EPA's six criteria pollutants (3).

Criteria Pollutant Monitoring

The TNRCC criteria pollutant monitoring network currently consists of 32 stations that monitor for ozone, sulfur dioxide, nitrogen dioxide, and carbon monoxide with continuous analyzers. The state network also includes 53 sites that measure PM_{10} or lead once every sixth day.

Measurements from these monitoring sites, as well as from 35 sites operated by local air pollution control programs in Houston, Dallas, Fort Worth, and El Paso, determine whether communities attain the NAAQS. Currently, the Houston-Galveston, Beaumont-Port Arthur, El Paso, and Dallas-Fort Worth areas do not attain the standard for ozone. El Paso does not attain the standard for carbon monoxide and PM_{10} .

Air Toxics Monitoring

In 1992, the TNRCC began deployment of an ambient air toxics monitoring network. The purpose of this network is to measure the long-term exposure of citizens to several speciated volatile organic air pollutants. The network currently includes 15 monitoring sites in 10 counties across Texas, which sample 19 different pollutants. Air toxics monitors are currently located in Clute, Brownsville, Dallas, Odessa, Midlothian, El Paso, Texas City, Channelview, Houston (three sites), Beaumont, Groves, Port Arthur, and Corpus Christi. Plans are to increase the

pollutant target list to 80 monitored compounds and to expand the number of monitoring sites to 50 by the end of 1995. Figure 1 depicts the air toxics monitoring sites operated by the TNRCC from October 1992 to September 1993.

Design of the network involved extensive community involvement through public meetings in all major urban areas in the state. Monitoring sites were selected based on numerous criteria including: pollution emissions within a 10-kilometer radius, prevalent wind direction, population density, degree of public concern, and traffic patterns around the site.

Each site consists of a shelter, a commercially available sampler, meteorological monitoring instrumentation, and a datalogger. Where available, samplers are housed in monitoring shelters containing other air quality monitoring instruments. Where such sites are not available, air toxics monitors are housed in smaller shelters, some of which are solar-powered.

Air samples are collected by agency field operators using evacuated 1-liter SUMMAR polished stainless steel canisters. The canisters are distributed to the field operators from the agency's central air toxics analytical laboratory in Austin, Texas. The Austin laboratory has certified them as clean by using a specialized cleaning apparatus in which the canisters are heated while being alternately evacuated and pressurized with ultrapure, humidified nitrogen, a process that takes several hours. The canisters are then analyzed to determine if any chemicals remain. If chemicals do remain, the canisters are recleaned until they meet specifications.

At the monitoring site, ambient air is continuously drawn into the canisters through a sampling train at a rate of $10\text{ cm}^3/\text{min}$ for a period of 24 hr from midnight to midnight every sixth day of the year. Sampling rate and collection period frequency are designed to allow the whole air sample to reach chemical equilibrium and provide a representative integrated sample for the area. At the end of the sample period, the sampler automatically seals the canister, which is then shipped back to the TNRCC's air toxics laboratory for analysis. The canister methodology was selected because of its broad use and acceptance by the U.S. EPA, other states, and the private monitoring networks in the state for ready data comparability. The compounds measured include benzene; bromomethane; 1,3-butadiene; carbon tetrachloride; chlorobenzene; chloroform;



Figure 1. Texas Natural Resource Conservation Commission air toxics monitoring sites from October 1992 to September 1993.

1,2-dibromoethane; 1,2-dichloroethane; 1,2-dichloropropane; ethyl benzene; methylene chloride; perchloroethylene; styrene; toluene; 1,1,1-trichloroethane; trichloroethylene; trichlorofluoromethane; vinyl chloride; and *o*-xylene.

The samples are analyzed by TNRCC staff in accordance with the U.S. EPA Method TO-14, using gas chromatography and mass spectrometry (ion trap) detection. A known volume of sample gas is passed through a cooling trap, condensing the volatile organic compounds (VOCs) onto the trap surface. The contents of the trap are heated and then swept onto a capillary column by a carrier gas where compounds are separated. Individual compounds are identified and quantified by mass spectrometry using an ion trap detector.

Public-Private Partnerships

In 1981, a group of industry leaders conceived a privately owned corporation that would operate an air monitoring network in the Houston area to provide air quality data to industry to help meet federal Prevention of Significant Deterioration (PSD) regulatory program requirements. The privately operated Houston Regional Monitoring (HRM) network has evolved to include eight monitoring sites that measure the criteria pollutants using continuous analyzers and 150 VOCs identified as ozone precursors and air toxics. The VOCs are collected using canister whole air samples and analyzed using a multidetector gas chromatographic analytical regime.

During the past 4 years, other industrial groups in Texas have initiated privately operated monitoring networks. The South East Texas Regional Planning Commission in the Beaumont area operates a five-station network. The Golden

Crescent monitoring network in the Victoria area operates four air toxics monitoring stations. The Texas City/La Marque monitoring network operates four air toxics and sulfur dioxide stations.

Private networks operate 43 monitoring instruments, local networks operate 63 instruments, and the TNRCC operates 135 total instruments in the state. This broad coverage of monitoring stations enables the state to provide valuable information on air quality trends. Figure 2 depicts the spatial coverage of both criteria and toxic pollutant monitoring stations for all monitoring networks along the Texas Gulf Coast.

Air Quality Trends in Texas

The sum of all of the monitoring data collected allows for extensive analysis of air quality data. Although no agency analysis has been focused on possible effects, specifically on asthma, trend analysis of pollutants related to the NAAQS is important since the NAAQS are established based on factors relating to asthma and other respiratory conditions. The discussion that follows focuses on the criteria pollutants significant to Texas because the standards have been exceeded in recent times.

Ozone

Ozone is the most pervasive pollutant in Texas as well as in the nation. High concentrations of ozone at ground level are a major health concern. The reactivity of ozone causes health problems because it damages lung tissue, reduces lung function, and sensitizes the lungs to other irritants. Scientific evidence indicates that ambient levels of ozone not only affect people with impaired respiratory systems, such as asthmatics, but healthy adults and children as well (4).

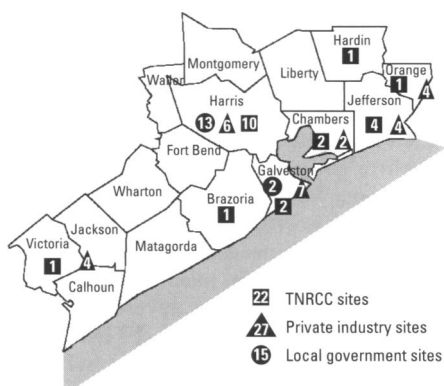


Figure 2. Criteria and toxic pollutant monitoring sites along the Texas Gulf Coast.

The NAAQS for ozone is 120 parts per billion (ppb) for a maximum daily 1-hr average. The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 120 ppb is equal to or less than 1 according to a methodology established by the U.S. EPA based on the amount of valid data collected. This standard has been described in a recent report by the National Academy of Sciences as highly sensitive to meteorological fluctuation and not reliable as a measure of progress in reducing ozone over several years for a given area (5). The U.S. EPA is currently reviewing the standard for ozone to determine if a more statistically robust standard would be appropriate.

In 1992, ozone levels were the lowest of the past 10 years throughout the United States (4). With the exception of El Paso, the number of days in which the ozone standard is exceeded has been decreasing over the past 10 years in the major metropolitan areas of Texas including Houston, Dallas, Fort Worth, and Beaumont-Port Arthur.

PM₁₀

Many studies have implicated particulate air pollution as contributing to the incidence and severity of respiratory disease (6,7). A national air quality standard has been set for particulate matter with an aerodynamic diameter equal to or less than 10 μm —PM₁₀. The U.S. EPA reports that annual mean concentrations have decreased 17% nationally between 1988 and 1992 (4). El Paso is the only city in Texas that has continued to exceed the NAAQS for PM₁₀.

Carbon Monoxide

Nationally, monitored carbon monoxide levels have decreased by 34% during the past 10 years as measured at the U.S. EPA's trend sites. The lowest annual mean for the past 10 years occurred in 1992 (4). Although El Paso remains in nonattainment for carbon monoxide, the number of times the standard has been exceeded has declined dramatically from 11 in 1992 to 2 in 1993. This decline is attributed to vehicle emission reductions from cleaner cars and the area's inspection/maintenance system.

Air Toxics Trends

The TNRCC air toxics monitoring network has been in operation for a relatively short time; therefore, no trend analysis has

been conducted on the data collected to date. However, measured VOC data from 1987 through 1993 from the HRM network has been analyzed by TNRCC statisticians for possible trends at the sites primarily influenced by industrial emissions. For each sampling date, 146 VOCs were measured and their concentrations reported in parts per billion by volume (ppbv) at each of the eight HRM monitoring sites. Sampling was conducted every sixth day. The analysis revealed a statistically significant 22% downward trend in all VOCs measured between 1987 and 1993 at Harris County industrial monitoring sites. This downward trend in levels of certain air pollutants is consistent with the reported TRI 15% reduction in on-site releases and off-site transfers for treatment, storage, and disposal of toxic pollutants in Texas from 1987 to 1992 recently announced by the U.S. EPA (T Porter and AM Gonzalez, personal communication).

Benzene

The volatile organic toxic compound of most concern in Texas is benzene. Texans are exposed to benzene every day. Benzene is a known human carcinogen and is commonly found at low concentrations in urban air. It is also the only air contaminant of its type that has been consistently measured above concentrations of concern in many major U.S. metropolitan areas. Benzene is emitted primarily from industrial and mobile sources. It is a significant component of gasoline and is released during industrial refining processes, during gasoline storage and transfer, and from benzene storage tanks. Mobile sources also emit benzene through evaporation during refueling and engine running losses. Mobile sources include both highway vehicles and off-road vehicles such as recreational, agricultural, and lawn and garden equipment. In Texas, the counties with the largest total point source benzene emissions are located along the Gulf Coast where there is a heavy concentration of petrochemical facilities. Figure 3 depicts the annual benzene point source emissions in Texas. Benzene measurements are made in both the private monitoring networks and the TNRCC air toxics network. Figure 4 shows the locations of TNRCC and HRM toxics monitoring sites and point sources of benzene that emit greater than 5 tons/year in Harris and Chambers counties.

Since there are no NAAQS for volatile organic toxic compounds, the TNRCC uses guidelines called "effects screening levels"

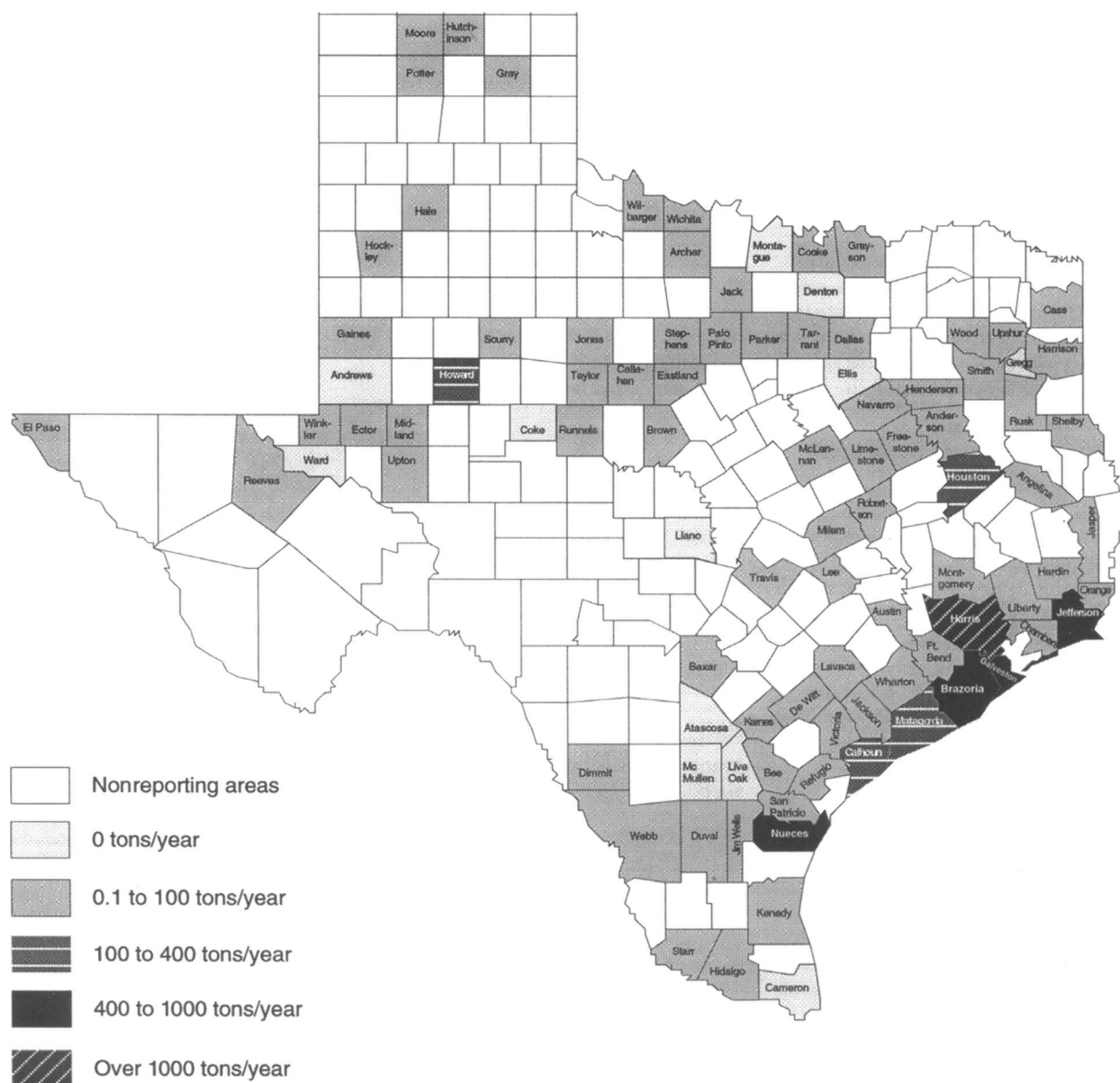


Figure 3. Annual benzene point source emissions. Source: TNRCC point source database derived from 1980, 1985, 1988, 1990, and 1992 emissions inventory questionnaire data.

(ESLs) that have been developed by TNRCC toxicologists for more than 2000 chemicals. These guidelines are usually 100 to 1000 times more stringent than the occupational standard for the same chemical.

During the first year of operation of the TNRCC Air Toxics Monitoring Network, October 1992 to September 1993, benzene was monitored at levels that exceeded its annual ESL of 1 ppbv at 8 of the 15 monitoring sites; benzene also exceeded its 24-hr ESL of 4 ppbv at 6 of the 15 sites (8). Figure 5 shows benzene levels at TNRCC

toxics monitoring sites from October 1992 to September 1993. Previous analysis of trend data from 1987 through 1990 showed a 44% decrease in measured benzene in the Houston area and a 48% decrease in benzene in the Beaumont–Port Arthur area (9).

A View to the Future

There is no one technology that addresses all monitoring needs. Current technologies for measuring the criteria pollutants are well established. Current technologies for

monitoring VOC emissions involve the use of time-integrated collection techniques such as canister and sorbent tubes that require gas chromatographic and mass spectrographic techniques or evolving real-time gas chromatographic techniques. Because of the need to measure multiple pollutants accurately, much interest is currently focused on the development of Fourier Transform Infrared (FTIR) multiple gas analyzers. The FTIR is a full spectrum instrument that is potentially capable of providing sensitive measurement of

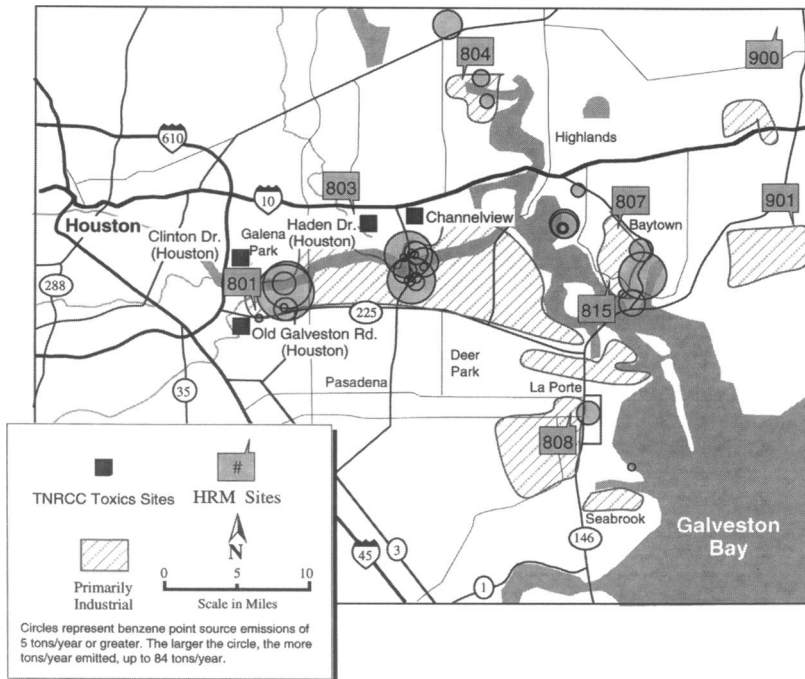


Figure 4. Texas Natural Resource Conservation Commission and Houston Regional Monitoring Network air toxics monitoring sites and point sources of benzene that emit greater than 5 tons/year in Harris and Chambers counties, Texas. Source: TNRCC point source database.

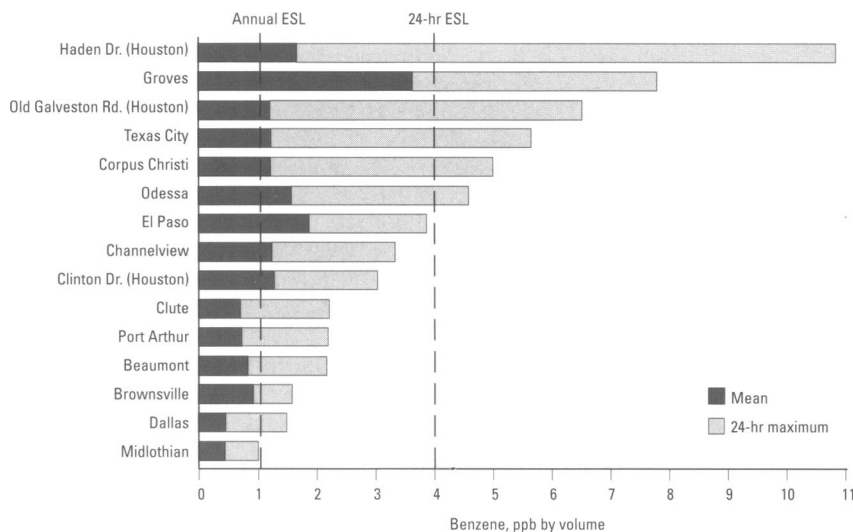


Figure 5. Benzene levels at Texas Natural Resource Conservation Commission air toxics monitoring sites from October 1992 to September 1993. Data from the TNRCC air toxics database.

many different gases with the same analyzer system. FTIR technology is based on the generation of an infrared light beam and measures absorption of specific

gas molecules in that beam. The FTIR can be configured as a continuous in-stack monitor, an ambient monitor, or a long path monitor in which the instrument

measures a time-integrated concentration over several hundred meters. FTIR is one of five optical techniques that have considerable potential for what is known as remote sensing. Differential optical absorption spectroscopy (DOAS), laser long path absorption (LLPA), differential absorption lidar (DIAL), and gas cell correlation techniques are also worthy of consideration (10).

Open path ultraviolet (UV/DOAS) monitoring is currently being used extensively in Europe to measure ozone, sulfur dioxide, and nitrogen dioxide. At this writing, the U.S. EPA approval is pending on a UV system in the United States.

The TNRCC is planning to purchase two FTIR systems during 1994. These systems will be used in the mobile monitoring program and deployed in a semipermanent monitoring station.

Federal Clean Air Act Programs

The 1990 Amendments included requirements for enhanced source monitoring so that sources can certify their emissions on an annual basis as part of the federal operating permit program. It is anticipated that some 7000 additional continuous in-stack monitoring systems will be required in Texas during the next few years.

In addition to source monitoring requirements, the Act requires additional ambient photochemical monitoring to drive the development of better science in understanding the ozone problem. Seven of these Photochemical Assessment Monitoring Stations (PAMS) will be deployed in Texas over the next 3 years.

Data Analysis and Additional Studies

Millions of hours of air quality measurements are made each year in Texas. Analysis of these data is a formidable task, and only recently has the state begun to add resources to statistically analyze these data in an other-than-cursory fashion. The TNRCC is now in partnership with Texas universities and such national organizations as the Southern Oxidants Study to provide greater insight into the scientific principles related to air pollution in Texas. Although the current database is expansive, additional air quality and meteorological information is needed. Current studies are being conducted to optimize the existing monitoring networks and to determine what additional monitoring is needed to meet the need for developing policy based on sound scientific measurements.

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