

The background of the entire page is a photograph of several tall industrial smokestacks or chimneys. They are silhouetted against a bright, hazy sky at sunset or sunrise, with a warm orange and yellow glow. Thick plumes of white smoke or steam are rising from the stacks, particularly from the one in the center. The stacks have various platforms, ladders, and pipes attached to them.

GRADE B

# Air Toxics

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## THE AIR TOXICS PROBLEM

A toxic air contaminant, or "air toxic," is an air pollutant which may contribute to mortality or serious illness, or pose other potential hazards to human health. Most air toxics are volatile and are found primarily in the atmosphere in the gaseous form but some occur in atmospheric particles or liquid droplets.

### The Magnitude of the Problem

- 189 Air Toxics on the Federal List
- 245 listed by the California EPA
- The U.S. EPA lists about 3,000 chemicals targeted for evaluation for pollution prevention action
- There may be more than 10,000 chemicals that require evaluation from a pollution prevention viewpoint

Toxic air contaminants originate from various chemical and manufacturing processes and can be released to the environment from a variety of controlled and uncontrolled sources ranging from automo-

biles to chemical manufacturing plants to consumer products. As a result, there is an enormous variation in the sources and ambient concentrations of air toxics on both local and regional scales.

Air toxics are of particular concern since they can be distributed over large regions, thus leading to population-wide exposure. With rapidly increasing population density, and robust growth in many industrial sectors, in Southern California the use of synthetic chemicals has escalated. For example, chemical solvents are used in paints, as degreasing agents in the automotive and aerospace industries, and by dry-cleaning establishments and auto repair shops. Synthetic chemicals are the building blocks of advanced materials such as plastic composites, and household pesticides and insecticides are used extensively. Despite their benefits many of these chemicals may also be harmful to human health and thus must be used cautiously.

Although a wide range of chemicals are an indispensable part of modern living, when they escape to the environment due to inadvertent releases, faulty equipment or poor handling, human exposure can result. To protect the public, a number of environmental regulations have been enacted to identify air

toxics, determine their sources, assess the amounts released to the environment, evaluate potential risk to the public and implement appropriate control strategies.

California is a pioneer in the area of air quality management. Aggressive programs to reduce emissions of carbon monoxide, oxides of nitrogen and sulfur, hydrocarbons and particulate matter have resulted in significant improvements in air quality in Southern California (1998 Report Card). However, these programs focus on the so-called "criteria pollutants" and were not designed to protect the public from chronic exposure to pollutants that could cause cancer or neurotoxic effects. The accident in Bhopal, India, which claimed 4000 lives and injured tens of thousands more in December 1984, was a watershed event in calling attention to the potentially devastating effects of massive releases of toxic chemicals. This event heightened concerns that protection measures were needed to reduce potential risk to the public from exposure to airborne toxic chemicals.

The passage of the 1990 Federal Clean Air Act was a milestone in environmental protection since, for the first time, specific chemicals and groups of chemicals were listed as hazardous air pollutants. Air





toxics were also regulated on the basis of integrated exposure assessment in which (Figure 1) all possible exposure pathways are considered.

Parallel legislation in California in the mid-1980's also established a statewide framework for evaluating and regulating potential toxic air contaminants. This legislation recognized that to protect the public from air toxics, it is necessary to understand their specific toxicity, source locations and emission rates, how they travel in the environment, how people are exposed, and the level of existing and potential health risks. The purpose of this article is to promote an understanding of the complexity of the air toxics problem in Southern California. Because of the enormous variation in the chemical, physical and health impact characteristics, as well as the origins of air toxics, devising properly encompassing health protection strategies is an enormous task we are only now beginning to address.

## SOURCES OF TOXIC AIR CONTAMINANTS

Air toxics are released to the environment from a variety of outdoor and indoor sources. Indoor releases result from activities such as cooking, use of home and garden supplies, releases from building materials and consumer products, as well as from tobacco smoke. In some cases, vehicular emissions can also lead to indoor contamination, as in houses that have attached garages. Although exposure to air toxics generated indoors can be significant in some cases, such emissions are currently not directly regulated.

Outdoor releases of air toxics are due to emissions from "mobile" sources such as automobiles, and from "stationary sources" such as manufacturing facilities, refineries, chemical production facilities, gasoline service stations, dry-cleaners, and other facilities that produce or utilize chemicals. It is important to note that, in Southern California vehicular emissions are a significant or even dominant contributor to emissions of certain air toxics including benzene and polycyclic aromatic hydrocarbons (PAHs). Mobile and stationary sources are considered intrinsically different from a reg-

ulatory viewpoint. In this article we focus only on stationary sources of air toxic emissions since such sources produce the largest number of different airborne toxic chemicals. We will treat air toxics from mobile sources, including diesel exhaust, in a future Report Card article.

In California, the identification, tracking, monitoring and assessment of public health risks due to air toxics are guided by two major Assembly Bills, AB 1807 and AB 2588, enacted in 1983 and 1987, respectively. The resulting California Air Toxics (CAT)



Figure 1: Multi-Pathway Exposures – inhalation, ingestion (food, water, soil), dermal

## Successful control of air toxic emissions requires a thorough understanding of emission sources and their distribution throughout the region.

Program, includes provisions to make the public aware of significant toxic exposures and to reduce risk. With the development of the CAT monitoring program, and the Federally mandated toxic release inventory (TRI), information on air toxic emissions from stationary sources has been mounting. Although these databases do not provide a complete reporting of all sources, they provide insights as to the relative distribution of various emitted air toxics and trends in their ambient levels.

The large number of listed air toxics makes it difficult to implement a uniform strategy to control their releases to the environment. For example, in Southern California, the emission profile for benzene (a known human carcinogen) by source category indicates that mobile sources contribute about 90% of the total benzene emissions (Figure 2). Therefore, even if all stationary sources were eliminated, exposure to benzene would only be reduced by about 10%. On the other hand, reduction in benzene levels in gasoline have resulted in reductions in ambient levels of benzene by more than a factor of two since 1990. This does not suggest that reducing benzene emissions from stationary sources is a less worthy goal. On the contrary, exposure to

benzene from stationary sources in the immediate vicinity of residential dwellings is of concern. For example, there are nearly 3000 gasoline dispensing stations distributed throughout the South Coast Air Basin (SoCAB). While their contribution to total emissions may be small, their impact on personal exposure can be significant.

An example of a strikingly different behavior is found for perchloroethylene (PERC), a solvent emitted from primarily dry-cleaning and degreasing operations in 1,300 facilities distributed throughout the SoCAB. These uses of PERC account for about 60% and 30% of its total emissions, respectively (Figure 3).

The above examples point out that successful control of air toxics emissions requires a thorough understanding of emission sources and their relative strength. Many individual sources of air toxics, such as dry cleaners, auto repair shops and metal plating facilities are small establishments scattered throughout Southern California, which do not have the resources needed to reduce fugitive emissions of air toxics. Clearly, controlling the multitude of these widely distributed facilities is a complex task requiring careful regulatory strategies.

Another example of distributed sources,

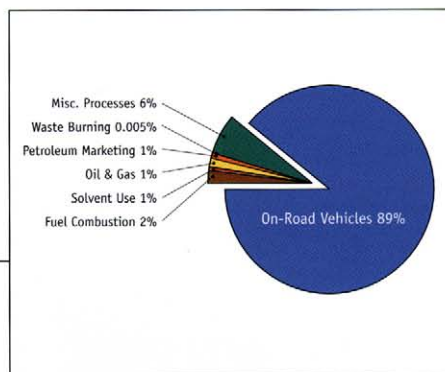


Figure 2: Benzene Emission Profile in Southern California (SCAQMD 1998).

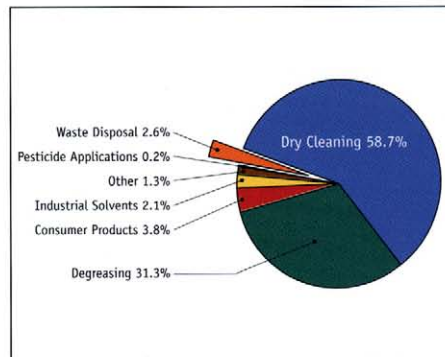


Figure 3: Perchloroethylene Emission Profile in Southern California (SCAQMD 1998).

albeit over a smaller area, is that of chemical or petrochemical production facilities, where fugitive emissions of volatile chemicals can occur as slow leaks from literally thousands of plant components. Detecting and controlling fugitive emissions from refineries and other large chemical manufacturing facilities represents a major technical challenge.



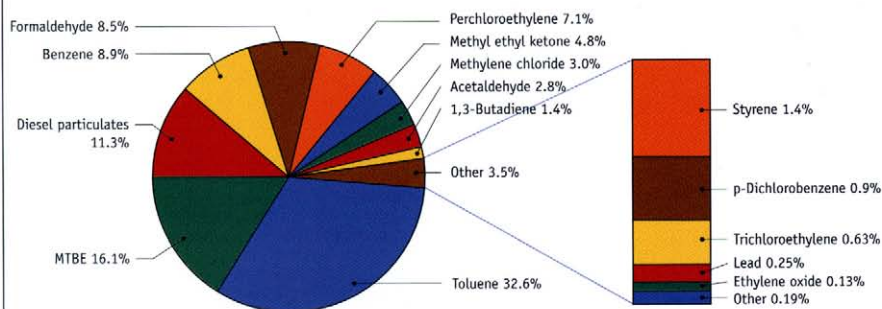


Figure 4: Distribution of emissions for 30 air toxics monitored in SoCAB (MATES-II).

Present programs of emission reporting do not account for all potential sources, necessitating ambient monitoring, along with air quality modeling, to improve emission estimates. In many cases, emissions reported under AB2588 account for only a small fraction of the total emissions. One of the striking findings of studies in the SoCAB is that of the 30 major air toxics evaluated by the South Coast Air Quality Management District (SCAQMD), diesel particulate (now regulated as an air toxic in California) contributes only about 11 % of the total emissions (Figure 4) but are claimed by the SCAQMD to be the major contributor (approximately 70%) of cancer health risks associated with air toxics. It is also important to realize that mobile sources constitute the major portion of the total releases of toluene, MTBE, diesel particulate, benzene, formaldehyde, acetaldehyde and 1,3-butadiene.

In reality, the small generators distributed throughout the basin (many of which

may be exempt from reporting) could contribute to local problems in their immediate neighborhoods. For example, a residential dwelling at the fence line of a small polluting facility may be affected to a degree not detected by intermittent monitoring or sampling removed from that specific source. Exemption of small generators does not make the problem of toxic "hot spots" go away; it simply hides potential local problems. It has been suggested that a monitoring system which is based on cumulative assessment of all potential sources would be most beneficial. Clearly such a system would also be more complex and costly to implement.

### WHAT HAPPENS TO AIR TOXICS ONCE RELEASED TO THE ENVIRONMENT?

Once released to the atmosphere, air toxics can rapidly disperse in the atmosphere and

can also transfer from the atmosphere to other media such as water, soil and vegetation. Air toxics which are volatile and sparingly water soluble (e.g., trichloroethylene, benzene and chloroform) are likely to be present mostly in the atmosphere. Chemicals with low vapor pressure are typically present in atmospheric particles which deposit to the terrestrial environment by dry deposition processes as well as by rain and snow scavenging. As a result, exposure to particle-bound chemicals (e.g., lead, PAHs and hexavalent chromium) can occur through multiple exposure pathways. Certain air toxics (e.g., PAHs, polychlorinated biphenyls, dioxins) can also accumulate, to a significant degree, in soil and vegetation. Thus, the intake of these contaminants via the food chain can be significant.

The migration of air toxics across the boundaries of environmental "media" (Figure 5) creates a "multimedia" problem. The major characteristics dictating the multimedia distribution of toxic air contaminants include their solubility in water, how volatile they are, and whether they tend to adsorb onto organic matter and bioaccumulate in living organisms. The persistence of air toxics in the environment is also affected by their chemical and biochemical transformations.

## Air toxics behave in a complex way in the environment. More than just air monitoring is required to assess their impact.

In general, the most significant degradation processes for organic air toxics occur in the atmosphere. Reactions with a variety of photooxidants can transform air toxics to other chemicals which can themselves be air toxics. Examples include the formation of formaldehyde and acetaldehyde from organic compounds, and nitro-PAHs from PAHs. Overall, the degradation of air toxics in the aquatic and terrestrial environments are typically less significant than in the atmosphere.

The atmosphere is the main "holding" reservoir for volatile toxic air contaminants with typically 80% or more of the total air toxic mass in the atmosphere. In contrast, the soil environment is the major "holding" reservoir for non-volatile air toxics. For example, more than 90% of the mass of benzo(a)pyrene present in the environment in the SoCAB, resides in the terrestrial environment.

Air toxics that have significant water solubility present another challenge. For example, MTBE, a gasoline additive which is now slated to be phased out, can pose a difficult groundwater remediation problem if it leaks from storage tanks. Groundwater contamination has also been caused by spills and leaks of other air toxics including aromatics and various chlorinated solvents.

The above examples illustrate the fact that air toxics behave in complex ways in the environment. More than just air monitoring is required to assess their impact. Monitoring of soil, vegetation and aquatic biota can also provide important indicators of the impacts of air toxics and improve risk exposure assessments.

### AMBIENT LEVELS OF AIR TOXICS

Monitoring of ambient levels of air toxics in Southern California began in 1986 with more intense monitoring of 31 specific air toxics undertaken since 1997 (Table 1). Data from both the California Air Resources Board (six monitoring stations in Southern California) and the SCAQMD (two intensive monitoring studies) demonstrate that during the 1990's there was an overall reduction in the ambient concentrations of the monitored air toxics. For example, there has been a steady decline in atmospheric concentrations of benzene and toluene (Figure 6). This improvement is attributed primarily to a reduction in mobile source emissions due to the introduction of reformulated gasoline. A decline in the ambient concentrations of chlorinated solvents and metals (chromium and lead) is also

Table 1: Monitored Air Toxics in SoCAB (MATES-II)

Benzene	Chloromethane
1,3 Butadiene	Formaldehyde
Dichlorobenzene (ortho- & para)	Acetaldehyde
Vinyl Chloride	Arsenic
Ethyl Benzene	Chromium
Toluene	Nickel
Xylene (m-, p-, o-)	Lead
Styrene	Cobalt
Carbon Tetrachloride	Copper
Chloroform	Manganese
Dichloroethane [1,1]	Phosphorous
Dichloroethylene [1,1]	Selenium
Methylene Chloride	Silver
Perchloroethylene	Zinc
Trichloroethylene	PAHs
	Elemental Carbon (Diesel Particulate)

apparent, although the improvement has been less dramatic.

The number of air toxics that have been monitored to date (Table 1) is only a small fraction of the total number currently listed. New air toxics are also being continuously identified. MTBE is an example of a chemical whose use was promoted rapidly by both government and the refinery industry, despite clear scientific evidence of its propensity to distribute in the environment and its potential toxicity. Recently, there has also been a growing concern with respect to potential cancer health risks associated with emissions from diesel engines. As noted earlier, it is now understood that diesel particulate represent "a toxic air pollutant" which may be the dominant carcinogen among all air toxics in the region.



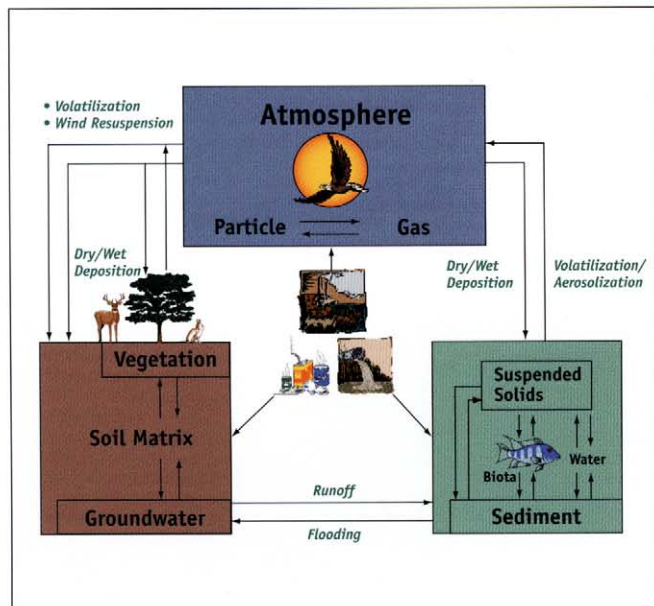


Figure 5: Chemicals do not stay where they originate. They tend to move across environmental phase boundaries.

Despite increased air monitoring efforts, there are numerous sources whose contribution remains unclear. For example, the concentrations of certain air toxics (e.g., benzene and PAHs) may be elevated near airports, but the contribution of airports to local exposure is not fully understood. There are also concerns with the health impact of air toxics which can form in the atmosphere. For example, PAHs can react in the atmosphere to form nitro-PAHs some of which can be more mutagenic or carcinogenic than the parent PAH. Future improvements in air quality should be sought by identifying air toxics that form in the atmosphere and developing appropriate public protection strategies.

contaminated crop, beef and dairy products (Figure 1). Air toxics which are suspected or known carcinogens are of most concern. Cancer health risks for specific air toxics can be estimated based on available monitoring data, toxicological information and model simulations. The cancer health risk is typically expressed as the number of excess cancer cases expected (number of people that will contract cancer) in a given population over a seventy year period, assuming that the entire population stayed in the region during this time period. Although there can be substantial uncertainties in health risk analysis, quantifying the risk helps to place the potential impacts of different air toxics in perspective.

## HEALTH RISKS

It is important to recognize that inhalation exposure to air toxics is directly proportional to ambient levels of these chemicals. However, total exposures from secondary routes can also be important as in the case of exposure to PAHs via ingestion of

Recent estimates of health risks by the SCAQMD suggest the 31 air toxics chemicals monitored in the basin contribute to a total cancer risk of about 1,400 per million people. Diesel particulate contribute about 70% of the total cancer health risks followed by other air toxics from mobile and stationary sources that combined contribute 20% and 10%, respectively. However, these estimates must be viewed with caution since only a fraction of the total number of air toxics has been monitored. Moreover, cancer potencies are not available for all of the listed air toxics. Consequently, uncertainties remains regarding the potential risk associated with the long list of air toxics that are still to be monitored.

## CONCLUSION AND GRADE

Data from air toxics monitoring, emissions reporting and modeling studies have yielded important information regarding the distribution of toxic air contaminants in Southern California, as well as the relative importance of their emission, and their contribution to cancer health risks. As a result, air quality management with respect to air toxics has improved over the past decade. For example, programs to reduce toxic air emissions from solvent use have resulted in measurable

## Air quality management with respect to air toxics has improved over the past decade.



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reduction in ambient concentrations. Reformulation of gasoline has also resulted in significant reduction in the ambient levels of certain air toxics. At present, it appears that on a regional scale air toxics from stationary sources are a relatively minor contributor to health risks in the SoCAB. But despite the progress made, emission inventories for air toxics are incomplete. Moreover,

information on the impact of local sources on personal exposure and identification of the most exposed population in the SoCAB is only beginning to emerge. In conclusion, we give a grade of B to regional efforts by the SCAQMD and CARB to monitor environmental concentrations, quantify potential health risks, and identify new air toxics.

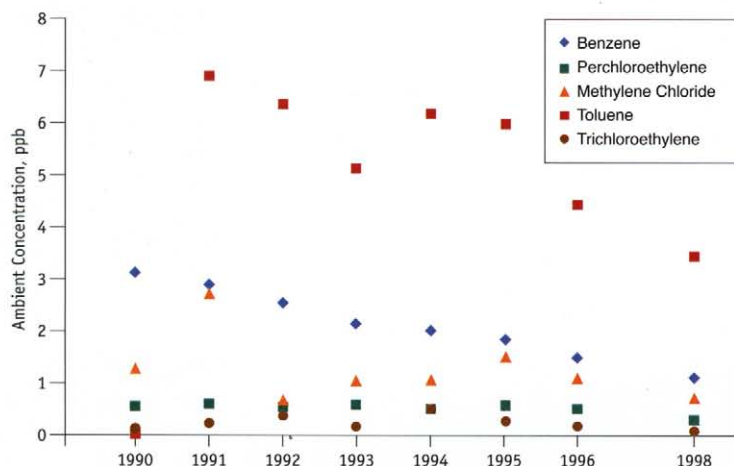


Figure 6: Average atmospheric concentrations of selected air toxics in the Los Angeles Basin. Source: ARB Air Quality Data and SCAQMD MATESII Draft Report