An Assessment of Air Toxics in Minnesota

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We used monitoring and modeling to assess the concentrations of air toxics in the state of Minnesota. Model-predicted concentrations for 148 hazardous air pollutants were from the U.S. Environmental Protection Agency Cumulative Exposure Project (1990 data). Monitoring data consisted of samples of volatile organic compounds, carbonyls, and particulate matter ≤ 10 µm in aerodynamic diameter collected at 25 sites throughout the state for varying periods of time (up to 8 years; 1991–1998). Ten pollutants exceeded health benchmark values at one or more sites by monitoring, modeling, or both (including acrolein, arsenic, benzene, 1,3-butadiene, carbon tetrachloride, chromium, chloroform, ethylene dibromide, formaldehyde, and nickel). Polycyclic organic matter also exceeded the benzo[a]pyrene health benchmark value assumed to represent this class of pollutants. The highest modeled and monitored concentrations of most pollutants were near the center of the Minnesota–St. Paul metropolitan area; however, many smaller cities throughout the state also had elevated concentrations. Where direct comparisons were possible, monitored values often tended to exceed model estimates. Upper-bound excess lifetime inhalation cancer risks were estimated to range from 2.7 × 10⁻⁴ to 140.9 × 10⁻⁴ (modeling) and 4.7 × 10⁻⁴ to 11.0 × 10⁻⁴ (using a smaller set of monitored carcinogens). Screening noncancer hazard indices summed over all end points ranged from 0.2 to 58.1 (modeling) and 0.6 to 2.0 (with a smaller set of monitored pollutants). For common sets of pollutants, the concentrations, cancer risks, and noncancer hazard indices were comparable between model-based estimates and monitored values.

The inhalation cancer risk was apportioned to mobile sources (54%), area sources (22%), point sources (12%), and background (12%). This study provides evidence that air toxics are a public health concern in Minnesota. Key words: air toxics, benzene, formaldehyde, modeling, monitoring, risk assessment, VOCs. Environ Health Perspect 108:815–825 (2000). [Online 24 July 2000] http://ehpnet1.niehs.nih.gov/docs/2000/108p815-825pratt/abstract.html

U.S. regulatory structure divides air pollutants into criteria pollutants and hazardous air pollutants (HAPs). The criteria pollutants include: carbon monoxide, nitrogen dioxide, sulfur dioxide, particulate matter (PM), lead, and ozone. These pollutants have been recognized for decades or longer as potential health and environmental threats. Hence, National Ambient Air Quality Standards (1), designed to protect human health and the environment, have been developed for these six pollutants.

The U.S. Clean Air Act (CAA) defines a HAP as an air pollutant to which no ambient air quality standard is applicable and which in the judgment of the Administrator [of the U.S. Environmental Protection Agency; EPA] causes, or contributes to, air pollution which may reasonably be anticipated to result in an increase in mortality or an increase in serious, irreversible, or incapacitating reversible illness. (2)

Only in recent years have the HAPs come under regulatory scrutiny. For example, the 1990 CAA Amendments listed 189 HAPs for which emission sources would be identified and technology-based emissions standards would be developed. Subsequent to the imposition of HAP emission standards, the U.S. Environmental Protection Agency (U.S. EPA) must conduct residual risk analyses to determine whether ambient concentrations continue to present unacceptable risks. The remaining hundreds to thousands of air pollutants that are neither criteria pollutants nor HAPs are virtually unregulated in the United States, although some are subject to various reporting or other requirements [e.g., the Toxics Release Inventory (3), the Toxic Substances Control Act (4), or Superfund (5)].

A growing number of reports have identified HAPs and other unregulated air pollutants as presenting a potential public health problem [e.g., (6–12)]. Based on these concerns, many states have begun monitoring concentrations of toxic air pollutants, and the U.S. EPA is planning a national monitoring network. In the United States, Minnesota began toxic air pollutants monitoring in 1991 and has expanded efforts in the intervening years. The publication of the U.S. EPA Cumulative Exposure Project (CEP) air modeling study (6,7), and the concerns that it raised, provided the incentive for undertaking a systematic analysis of existing data on toxic air pollutants in Minnesota. Documentation of the complete analysis can be found in the Minnesota Pollution Control Agency (MPCA) Staff Paper on Air Toxics (13). This paper comprises the highlights of the staff paper. Both monitoring and modeling information are included. The monitoring data are measurements taken at sites in the MPCA air toxics monitoring network. The modeling information was obtained from the U.S. EPA CEP (6,7) and analyzed in detail for Minnesota.

Methods

Modeling. We obtained the Minnesota CEP modeling results from the U.S. EPA. The details of the CEP study are presented elsewhere (6-8,14). Briefly, 1990 emissions of 148 air toxics were estimated from existing databases for point, area, and mobile sources. Point source locations were resolved specifically; however, mobile and area source emission inventories were generally available only to the county level. These emissions were apportioned to census tracts through weighting by population, roadway miles, railway miles, or land use, depending on the specific emission category. U.S. EPA investigators caution against over-reliance on the spatial resolution of the CEP results.

U.S. EPA investigators used the Assessment System for Population Exposure Nationwide model (15) to predict annual average concentrations in each census tract. The model uses a Gaussian plume algorithm and climatologic data to estimate long-term average concentrations. When monitoring data were available on concentrations of specific pollutants in remote areas not influenced by the modeled sources, these background concentrations were added to the modeled values. Emissions sources in Minnesota were not identified for all of the 148 pollutants; however, concentrations of all 148 substances were estimated. Some modeled pollutant concentrations were zero, some pollutants were transported into the state, some pollutants were formed secondarily, and some modeled concentrations were increased by incorporation of background concentrations. We included only a subset of the 148 CEP pollutants in this analysis (Table 1). We included pollutants if they...
were monitored by the MPCA or if concentration estimates were non-zero and a health benchmark value was available.

Several of the modeled pollutants may be formed secondarily in the atmosphere (e.g., via photochemical reactions). U.S. EPA investigators identified precursors for these pollutants and selected decay rates from the literature. They then conducted model runs for precursor-product pairs in which the pollutant product concentration was incremented according to the decay of the precursor. This method resulted in a partial accounting of secondary pollutant formation.

**Monitoring.** The MPCA operates a statewide network of toxic air pollution monitoring sites (Figure 1 and Table 2) that developed over several years to address multiple concerns. Some sites were established to measure concentrations in the vicinity of specific point sources. Other sites were established to

| Pollutant                  | No. | Median | Mean | Maximum | LDL | Values < LDL (n) | Cancer benchmark | Noncancer benchmark |
|----------------------------|-----|--------|------|---------|-----|------------------|------------------|--------------------|
| **Carbonyls**              |     |        |      |         |     |                  |                  |                    |
| Acetaldehyde               | 2,479 | 0.99  | 1.14 | 8.76    | 0.009 | 0                | 5                | M DH IHRV          |
| Acetone                    | 2,479 | 1.62  | 1.84 | 7.96    | 0.015 | 16               | -                | -                  |
| Acrolein                   | -    | -     | -    | -       | -    | -                | -                | -                  |
| Benzaldehyde               | 2,377 | 0.16  | 0.22 | 2.83    | 0.009 | 562              | -                | -                  |
| Butyraldehyde              | 2,478 | 0.28  | 0.35 | 3.41    | 0.011 | 7                | -                | -                  |
| Crotonaldehyde             | 2,478 | 0     | 0.06 | 1.62    | 0.009 | 2,142            | -                | -                  |
| Formaldehyde               | 2,494 | 1.37  | 1.7  | 20.99   | 0.048 | 0.8              | 23               | M DH IHRV          |
| Propanaldehyde             | 2,479 | 0.17  | 0.2  | 1.39    | 0.012 | 108              | -                | -                  |
| **VOCs and other nonmetals and noncarbonyls** | | | | | | | | |
| Acetonitrile               | -    | -     | -    | -       | -    | -                | -                | -                  |
| Acrylamide                 | -    | -     | -    | -       | -    | -                | 0.008            | U.S. EPA IRIS      |
| Acrylic acid               | -    | -     | -    | -       | -    | -                | -                | 1.0                |
| Acrylonitrile              | -    | -     | -    | -       | -    | -                | 0.1              | M DH IHRV          |
| Aniline                    | -    | -     | -    | -       | -    | -                | 6                | Cal OEHHA          |
| Benzene                    | 3,650 | 1.32  | 1.81 | 26.35   | 0.25 | 41               | 1.3-4.5          | M DH IHRV          |
| Bromoform                  | -    | -     | -    | -       | -    | -                | 9                | U.S. EPA IRIS      |
| Bromomethane               | 2,507 | 0.06  | 0.08 | 2.61    | 0.045 | 815              | -                | -                  |
| 1,3-Butadiene              | -    | -     | -    | -       | -    | -                | 0.04             | M DH IHRV          |
| Carbon disulfide           | -    | -     | -    | -       | -    | -                | 700              | M DH IHRV          |
| Carbon tetrachloride       | 3,650 | 0.77  | 0.72 | 1.48    | 0.19 | 113              | 0.7              | U.S. EPA IRIS      |
| CFC-11                     | 2,507 | 1.76  | 2.29 | 69.03   | 0.24 | 8                | 30.0             | U.S. EPA HEAST     |
| CFC-113                    | 2,507 | 0.7   | 1.91 | 206.35  | 0.86 | 1,969            | -                | -                  |
| CFC-114                    | 2,507 | 0.09  | 0.11 | 0.98    | 0.09 | 1,228            | -                | -                  |
| CFC-12                     | 2,188 | 2.95  | 2.95 | 16.7    | 0.11 | 0                | 0.1              | U.S. EPA IRIS      |
| Chlorodane                 | -    | -     | -    | -       | -    | -                | 0.7              | U.S. EPA IRIS      |
| Chlorobenzene              | 3,650 | 0.06  | 0.08 | 6.22    | 0.24 | 3,477            | -                | 200                |
| Chloroform                 | 3,650 | 0.11  | 0.14 | 6.91    | 0.11 | 2,205            | 0.4              | U.S. EPA IRIS      |
| Cumene                     | -    | -     | -    | -       | -    | -                | 700              | M DH IHRV          |
| 1,2-Dichlorobenzene        | 2,507 | 0.11  | 0.14 | 2.1     | 0.13 | 1,305            | -                | U.S. EPA HEAST     |
| 1,3-Dichlorobenzene        | 3,650 | 0.11  | 0.22 | 8.51    | 0.37 | 3,144            | -                | -                  |
| 1,4-Dichlorobenzene        | 2,507 | 0.22  | 0.29 | 4.13    | 0.19 | 1,058            | -                | -                  |
| 1,1-Dichloroethane         | 3,650 | 0.02  | 0.02 | 1.46    | 0.08 | 3,428            | 6                | Cal OEHHA          |
| 1,2-Dichloroethane         | 3,650 | 0.04  | 0.05 | 3.15    | 0.09 | 3,081            | 0.4              | U.S. EPA IRIS      |
| 1,2-Dichloroethylene       | 3,650 | 0.02  | 0.02 | 2.18    | 0.1  | 3,531            | -                | Cal OEHHA          |
| Dichloromethane            | 3,650 | 0.27  | 0.49 | 46.24   | 0.19 | 1,141            | 2.0              | M DH IHRV          |
| 1,2-Dichloropropane        | 2,507 | 0.02  | 0.02 | 1.38    | 0.1  | 2,249            | -                | -                  |
| cis-1,3-Dichloropropene    | 2,507 | 0    | 0.02 | 0.99    | 0.14 | 2,464            | 0.3              | U.S. EPA HEAST     |
| trans-1,3-Dichloropropene  | 2,507 | 0    | 0.03 | 1.48    | 0.21 | 2,425            | 0.3              | U.S. EPA HEAST     |
| Ethyl benzene              | 3,650 | 0.46  | 0.74 | 21.02   | 0.22 | 726              | -                | -                  |
| Ethyl chloride             | -    | -     | -    | -       | -    | -                | -                | 1,000              |
| Ethylene dibromide         | 3,650 | 0.02  | 0.04 | 14.68   | 0.32 | 3,612            | 0.05             | M DH IHRV          |
| Ethylene glycol            | -    | -     | -    | -       | -    | -                | 10,000           | U.S. EPA IRIS      |
| Methyl chloride            | -    | -     | -    | -       | -    | -                | -                | -                  |
| Methyl diphenyl isocyanate | -    | -     | -    | -       | -    | -                | -                | -                  |
| Methyl ethyl ketone        | -    | -     | -    | -       | -    | -                | -                | -                  |
| Methyl isobutyl ketone     | -    | -     | -    | -       | -    | -                | -                | -                  |
| Methyl methacrylate        | -    | -     | -    | -       | -    | -                | -                | -                  |
| Methyl tertiary butyl ether| -    | -     | -    | -       | -    | -                | -                | -                  |
| Naphthalene                | -    | -     | -    | -       | -    | -                | -                | -                  |
| Phthalic anhydride         | -    | -     | -    | -       | -    | -                | -                | -                  |

*continued, next page*
Given these multiple purposes, it is clear that there are biases in the data which should be recognized in its interpretation. These biases include changes in analytical techniques, an unequal number of data points per location, different time frames for different sites, different site selection criteria, and a nonuniform spatial distribution of sampling locations. These biases also limit the types of statistical analyses that can be undertaken, and they must be borne in mind when interpreting the data. We note such considerations as necessary. A more complete description of the site locations and sample collection periods is given in the staff paper (13).

Three types of samples were collected at each site: volatile organic compounds (VOCs), carbonyls, and particulate matter \( \leq 10 \mu m \) in aerodynamic diameter (PM10). The metal measurements were of total elemental concentration. Where noted in brackets the toxicity values apply to the indicated form of the metal.

We collected carbonyl samples every sixth day (24-hr samples) following U.S. federal reference method TO-11A (19). Originally, beginning in 1991, only formaldehyde was determined; however, beginning in 1995 six additional carbonyls (acetaldehyde, acetone, benzaldehyde, butyraldehyde, crotonaldehyde, and propionaldehyde) were determined. A 1-month test in April 1995 found that up to 50% of collected formaldehyde was lost when ambient ozone concentrations were elevated. After this test, beginning in May 1995, a section of Teflon tubing containing granulated potassium iodide was added to the carbonyl sampling trains to remove ozone. The early carbonyl data (before May 1995) were not adjusted to account for losses due to degradation by ozone because ozone measurements were not available at the monitoring sites. As a result the carbonyl data cannot be considered comparable before and after this change in monitoring technique. With the exception of the formaldehyde trend collect baseline data on air toxics concentrations in the M inneapoli-st Paul metropolitan (metro) area. A third group of sites was established as part of a legislatively mandated statewide air toxics monitoring network (SATMN) (16). The objective of the SATMN study was to collect 1-year snapshots of concentrations at sites throughout the state. These sites were randomly selected with weighting for geographic coverage and population density. All sites were located at rooftop level and away from immediate pollution sources following guidance provided by the U.S. EPA (17).

### Table 1

| Pollutant                  | No. | Median | Mean   | Maximum | Values < LDL (n) | Cancer benchmark | Noncancer benchmark |
|---------------------------|-----|--------|--------|---------|------------------|------------------|---------------------|
| 2,3,7,8-TCDD              |     |        |        |         |                  |                  |                     |
| POM [Bag/p surrogate]     |     |        |        |         |                  |                  |                     |
| Propylene oxide           |     |        |        |         |                  |                  |                     |
| Styrene                   |     |        |        |         |                  |                  |                     |
| 1,1,1,2-Tetrachloroethane |     |        |        |         |                  |                  |                     |
| Tetrachloroethylene       |     |        |        |         |                  |                  |                     |
| Toluene                   |     |        |        |         |                  |                  |                     |
| Toluene disiocyanate      |     |        |        |         |                  |                  |                     |
| 1,1,1- Trichloroethane    |     |        |        |         |                  |                  |                     |
| 1,1,2- Trichloroethane    |     |        |        |         |                  |                  |                     |
| Trichloroethylene         |     |        |        |         |                  |                  |                     |
| 1,2,4-Trimethylbenzene    |     |        |        |         |                  |                  |                     |
| 1,3,5-Trimethylbenzene    |     |        |        |         |                  |                  |                     |
| Vinyl acetate             |     |        |        |         |                  |                  |                     |
| Vinyl chloride            |     |        |        |         |                  |                  |                     |
| Vinylidene chloride       |     |        |        |         |                  |                  |                     |
| Xylenes                   |     |        |        |         |                  |                  |                     |
| m,p-Xylene                |     |        |        |         |                  |                  |                     |
| n-Xylene                  |     |        |        |         |                  |                  |                     |
| PM10 meteals              |     |        |        |         |                  |                  |                     |
| PM2.5                     |     |        |        |         |                  |                  |                     |
| Antimony [trioxide]       |     |        |        |         |                  |                  |                     |
| Arsenic                   |     |        |        |         |                  |                  |                     |
| Beryllium                 |     |        |        |         |                  |                  |                     |
| Cadmium                  |     |        |        |         |                  |                  |                     |
| Chromium [VI]             |     |        |        |         |                  |                  |                     |
| Cobalt                    |     |        |        |         |                  |                  |                     |
| Copper                    |     |        |        |         |                  |                  |                     |
| Lead                     |     |        |        |         |                  |                  |                     |
| Manganese                |     |        |        |         |                  |                  |                     |
| Mercury [elemental]       |     |        |        |         |                  |                  |                     |
| Nickel [substitutes or compounds] |     |        |        |         |                  |                  |                     |

### Notes

The summary statistics include data from all sites and all times combined. All concentrations are in micrograms per cubic meter. Pollutants with missing monitoring data (dashes) are included because the health benchmarks were used in the analysis of the modeling data. Abbreviations: Cal OEHHA, California Office of Environmental Health Hazard Assessment; HEAST, Health Effects Assessment Summary Tables; IHRV, inhalation health risk value; IRIS, Integrated Risk Information System; MDH, Minnesota Department of Health.

*The cancer health benchmarks are based on the MDH tolerable risk level of \( 1 \times 10^{-5} \). The data sources are defined in more detail in the text. The tetrachloroethylene benchmark is provisional only and has not been through the U.S. EPA formal review process. The metal measurements were of total elemental concentration. Where noted in brackets the toxicity values apply to the indicated form of the metal.
analysis, the carbonyl data reported here include only samples collected with ozone scrubbing (after May 1995).

Beginning in 1996, we also collected 24-hr PM$_{10}$ samples every sixth day at each site in accordance with the U.S. federal reference method for PM$_{10}$ (20). After gravimetric analysis, a 47-mm disk was cut from each filter at a random location. The disks were analyzed for metals using energy dispersive X-ray fluorescence (XRF) (Spectrace Quan-X model 8000; Spectrace Instruments, Fort Collins, CO, USA). The measurement methodology is capable of determining 33 elements. We report data on the 11 metals included in the CEP analysis plus copper and zinc. We do not report data on the remaining metals because of detection limit issues.

Method detection limits are not reported because some of the analytes are not detected in a large fraction of the samples, making it difficult to calculate the method detection limit. Instrument detection limits are available but are not reported here. We report lower detection limits (LDLs) (Table 1) that were determined using various methods. For VOCs and carbonyls a standard was prepared to 5 times the estimated LDL. We made seven replicate measurements of the standard, and the LDL was taken as the standard deviation of the replicate analyses divided by the square root of $n$, and this quantity was multiplied by the Student’s $t$-value appropriate for a 99% confidence level with $n - 1$ degrees of freedom.

For metals analysis using XRF, we determined the LDL using guidance provided by Spectrace Instruments, according to which an element’s peak is detected above background with 99% confidence if the peak counts are greater than 3 times the square root of the background counts. Thus the LDL can be calculated from analysis of a standard filter using the following equation:

$$\text{LDL} = \frac{3 	imes (I_b)^{1/2}}{I_p} \times \frac{1}{T^{1/2}} \times \text{concentration},$$

where $I_b$ = background (counts per second (cps)), $I_p$ = peak (cps), and $T$ = lifetime under specified excitation condition.

In the case of several metals, a large fraction of the measurements were below the LDL. Table 1 shows the number of values below the LDL for each monitored substance. In addition, because the reading from a blank was subtracted from each measurement, there are some negative values in the data, particularly the metals data. These negative values and values below the LDL could be censored in some way, such as converting them to zero (or one-half the LDL). The best method for treating such data is a matter of debate in the scientific literature. We chose to retain all of the raw values in the data for the statistical analyses reported here, including values below detection, zeroes, and negative values. Statistical analyses were done using SPSS (SPSS, Inc., Chicago, IL, USA).

The number of negative values was low in the VOC and carbonyl data (butyraldehyde, 4 negative values; acetone, 13; and CFC-113, 1); thus any censoring of the negative values would have a negligible effect. On the other hand, there were many negative values in the metals data (As, 68; Cd, 201; Cr, 160; Cu, 12; Mn, 59; Ni, 304; Pb, 132; Se, 146; Zn, 21). Negative values were always close to zero. Given the large number of negative values, censoring the negative data would affect the reported values for many of the metals. For example, replacing all negative values with zero would raise the mean value slightly.

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**Figure 1.** Monitoring site locations in Minnesota. Abbreviations: acad, academy; Mpls, Minneapolis.
Health benchmarks. The concentrations calculated from monitoring and modeling data were subsequently compared to cancer and chronic noncancer health benchmarks (Table 1). The noncancer benchmarks were defined as concentrations of a pollutant in the ambient air below which there is likely to be no public health concern over a lifetime of exposure. The cancer benchmarks were defined as the pollutant concentrations of a value of $1 \times 10^{-3}$ upper-bound excess lifetime inhalation cancer risk for an adult.

The health benchmarks used in this study were derived from several sources. The primary source of benchmarks was the Minnesota Department of Health (MDH) draft inhalation health risk values (IHRVs) (21). The draft IHRVs consist of both noncancer and cancer benchmarks. The second source of benchmarks was the U.S. EPA reference concentrations and inhalation unit risks from the Integrated Risk Information System (IRIS) (22) and the Health Effects Assessment Summary Tables (23). If values from these sources were not available, we used inhalation unit risks and proposed inhalation reference exposure levels from the California Office of Environmental Health Hazard Assessment (24). Pollutants that did not have a health benchmark from one of these sources were not evaluated for potential public health concerns. The health benchmark values presented here are the values from the various data sources as of December 1999. Although the absolute magnitude of the risks represented by the benchmark values are uncertain, these values nevertheless provide some guidance against which to evaluate the modeled and measured air concentrations.

The draft MDH IHRV for hexavalent chromium was used as the health benchmark value for chromium despite the fact that both the modeled emissions estimates and the measured concentrations were for total chromium. The Cr-VI IHRV is based on the IRIS unit risk value, which is based on a study of lung cancer rates in chromate workers (25). The lung cancer deaths were “related to insoluble (trivalent), soluble (hexavalent), and total chromium exposure” (25), but the identification of the specific form of chromium responsible for the lung cancer was uncertain. Given the evidence of other studies, the unit risk was developed under the assumption that cancer mortality was due to Cr-VI, and it is further assumed that Cr-VI was not less than one-seventy the concentration of total Cr (25). It is unknown how the ratio of Cr species in ambient air compares to that of the worker’s exposure in the epidemiologic study, although it is possible that there is a higher ratio of the less toxic trivalent form in the atmosphere because hexavalent chromium may react atmospherically to form trivalent chromium (26). Because of the limited knowledge on the ambient air species of chromium, it is unknown to what extent the use of the hexavalent chromium health benchmark value may overstate the human health risk due to inhalation of total chromium.

Results and Discussion

Based on modeling, the concentrations of eight pollutants (acrolein; arsenic; benzene; 1,3-butadiene; carbon tetrachloride; formaldehyde; and nickel) exceeded health benchmark values in one or more census tracts in Minnesota (Table 3). POM is a class of pollutants that could also be considered to exceed a surrogate health benchmark. Because there is no health benchmark for this class of pollutants, an assumption was made that the health benchmark value for benzo[a]pyrene [B(a)P], an important constituent of POM, could provide a surrogage value for estimating the toxicity of POM. B(a)P appears to be one of the more toxic components of POM, but it is unknown at present whether this assumption would result in a systematic under- or overestimation of toxicity.

The CEP study estimated POM emissions using speciation profiles that were compiled from several studies using a variety of methods, and no precise definition of chemical species and relative concentrations is available. Although a complete breakdown of the individual compounds that make up the POM modeled in the CEP study is not possible, PAHs and related compounds are expected to be strongly represented. The CEP emissions breakdown by source category was point sources, 11%; area sources, 26%; and mobile sources, 63%. POM is not expected to exist as separate individual species, but instead is typically found in association with particles of heterogeneous composition.

The California Air Resources Board investigated B[a]P as a toxic air contaminant (27) and compared potency equivalency factors (PEFs) of 24 polycyclic aromatic hydrocarbons (PAHs) with the PEF for B[a]P. Of the 24 PAHs, all of which can be components of POM, 13 PEFs were lower than B[a]P, seven were higher than B[a]P, and four were equal to B[a]P.

The California Air Resources Board also established a human cancer potency unit risk value for diesel exhaust [3 × 10⁻⁴ (µg/m³)⁻¹] that is similar to its value for B[a]P [1.1 × 10⁻³ (µg/m³)⁻¹] (28). Although POM and diesel particulate matter are not identical, the two categories have several similarities. Diesel particulate matter consists of a solid core composed mainly of carbon, a soluble organic fraction, sulfates, and trace elements.

Table 3. Pollutant benzene number of census tracts exceeding health benchmark (%) Number of monitoring sites with median exceeding health benchmark (%)

| Pollutant | Number of census tracts exceeding health benchmark (%) | Number of monitoring sites with median exceeding health benchmark (%) |
|-----------|------------------------------------------------------|---------------------------------------------------------------|
| Acrolein  | 855 (70)                                             | Not monitored                                               |
| Arsenic   | 56 (5)                                               | ?                                                           |
| Benzene   | 575 (47)                                             | 9 (36)                                                      |
| 1,3-Butadiene | 742 (60)  | Not monitored                                            |
| Carbon tetrachloride | 1,230 (100) | 22 (88)                                                   |
| Chloroform | 0 (0)                                               | 1 (4)                                                       |
| Chromium | 9 (1)                                                | ?                                                           |
| Ethylene dibromide | 0 (0)     | 1 (4)                                                      |
| Formaldehyde | 701 (57)    | 23 (92)                                                    |
| Nickel   | 5 (10³)                                              | ?                                                           |
| POM      | 1,230 (100)                                          | Not monitored                                               |

*The status of the monitored metals is uncertain due to the large fraction of values below the LDL. **The modeled exceedance of the nickel health benchmark is questionable (see text).
(29). Typically, approximately 25% of diesel particles consist of extractable organics (although the range may be 5–90%), consisting of 14–35 carbon open-chain hydrocarbons, alkyl-substituted benzenes, and PAH derivatives (29). The toxicity of diesel particles is determined by the particle size and composition. The PAH derivatives within the soluble organic fraction of diesel particles are expected to be similar to POM.

The U.S. EPA estimated the 95% upper confidence limits of the lifetime risk of cancer from inhalation of 1 µg/m³ diesel particulate matter. The values from various studies ranged from $1.6 \times 10^{-2}$ to $3.5 \times 10^{-6}$ (30–32). On this same scale the B[a]P potency would be $9 \times 10^{-4}$, which is in the middle of the range of values for diesel particulate matter. A final assessment of the toxicity of POM awaits further work; however, based on the weight of this partial evidence, we suggest that the use of B[a]P toxicity as a surrogate for POM more likely approximates the total inhalation risk from the modeled pollutants than not including POM at all.

Table 4 lists the total emissions from the CEP inventory, along with the percentages that were apportioned to point, area, and mobile sources. The CEP study did not include a category for nonanthropogenic emissions, but background concentrations were estimated. Table 4 shows the percentage of the statewide mean concentrations that were made up of background concentrations. Four of the pollutants of greatest concern (i.e., those exceeding a health benchmark at some location: benzene; 1,3-butadiene; formaldehyde; and POM) were emitted predominantly from mobile sources. The three metals of concern in the modeling analysis (As, Cr, and Ni) were emitted predominantly from mobile sources. The three metals of concern in the modeling analysis (As, Cr, and Ni) were emitted predominantly by point sources. The pattern of geographic distribution of modeled concentrations of As, Cr, and Ni appeared to follow a pattern of higher concentrations near known point sources.

Although Table 4 shows that acrolein emissions were attributed mainly to area sources, acrolein is an important degradation product of other pollutants like benzene and 1,3-butadiene (33,34) that are emitted primarily from mobile sources. A full accounting of secondary pollutant formation would likely show that mobile source emissions of acrolein are of greater importance than shown in the Table 4. Similarly, although Table 4 shows that carbon tetrachloride is emitted predominantly from area sources, in fact it is emitted only in very small amounts, and the predominant source of the model estimated concentrations was background concentrations. Carbon tetrachloride concentrations were elevated throughout the state, with little geographic variation. Although there is some present-day usage from preexisting stocks of carbon tetrachloride and there may still be some limited production, it is a long-lived gas that has been mostly phased out of production under the Montreal Protocol on ozone-depleting substances, and the values presented here are believed to represent a global background due mainly to historical emissions (35).

Figure 2 is a map of Minnesota showing the modeled concentrations of 1,3-butadiene. Concentrations were highest in the center of the metro area and decreased with distance from there. In addition, concentrations

| Pollutant                  | Total emissions (tons/day) | Point source contribution (%) | Area source contribution (%) | Mobile source contribution (%) | Background concentration as percent of modeled mean concentration (%) |
|----------------------------|---------------------------|-------------------------------|-----------------------------|-------------------------------|---------------------------------------------------------------------|
| Acrolein*                  | 2.13                      | -                             | 64                          | 36                            | 0                                                                   |
| Arsenic                    | 0.09                      | 94                            | 4                           | 2                             | 0                                                                   |
| Benzene                    | 25.76                     | 5                             | 28                          | 67                            | 32                                                                 |
| 1,3-Butadiene              | 3.89                      | 2                             | 32                          | 66                            | 0                                                                   |
| Carbon tetrachloride       | 0.04                      | 42                            | 58                          | -                             | 100                                                                |
| Chloroform                 | 0.34                      | 83                            | 17                          | -                             | 94                                                                 |
| Chromium                  | 0.07                      | 83                            | 12                          | 5                             | 0                                                                   |
| Ethylene dibromide         | 0.00                      | -                             | -                           | -                             | 100                                                                |
| Formaldehyde*              | 15.40                     | 9                             | 33                          | 58                            | 26                                                                 |
| Nickel                    | 0.18                      | 77                            | 19                          | 4                             | 0                                                                   |
| POM                       | 3.79                      | 3                             | 30                          | 67                            | 0                                                                   |

Data taken from the CEP study results for Minnesota. Secondary formation of these pollutants may contribute significantly, thereby altering the indicated source contributions.

Figure 2. Modeled 1,3-butadiene concentrations in Minnesota. The lightest shaded areas are below the 1,3-butadiene health benchmark value of 0.04 µg/m³.
exceeded the health benchmark value at numerous smaller cities. This pattern of geographic distribution was also found for modeled concentrations of acrolein, benzene, formaldehyde, and POM and appears to be characteristic of pollutants emitted mainly from mobile sources.

We estimated the total upper-bound excess lifetime inhalation cancer risk from the combination of all of the modeled pollutants by summing the cancer risk from individual carcinogens. The calculation was done separately for each census tract. Figure 3 is a map showing the results for the metro area. Upper-bound excess lifetime cancer risks based on modeled concentrations ranged from $2.7 \times 10^{-3}$ to $140.9 \times 10^{-3}$. These modeled risks can be apportioned to source categories as shown in Figure 4. This apportionment includes the assumption that the risk from POM can be approximated using the surrogate of B[a]P. It should also be noted that the risk apportionment in Figure 4 represents that for an apocryphal individual who is exposed to pollutant concentrations averaged across all of the census tracts in the state. A specific person’s risk will differ. For example, a person living at the fenceline of a point source or next to a gas station may have a higher risk from point or area sources, respectively.

Figure 5 shows the apportionment among individual pollutants of the upper-bound excess lifetime cancer risk of an average Minnesotan. This apportionment also includes the assumption that the risk from POM can be approximated using the surrogate of B[a]P. POM accounted for 60% of the risk, clearly overshadowing all other pollutants. Benzene; 1,3-butadiene; carbon tetrachloride; chromium; and formaldehyde each accounted for 5% or more of the risk.

Figure 3. Estimated upper-bound excess lifetime cancer risk from inhalation of 30 modeled pollutants. This figure includes the assumptions that all chromium is hexavalent chromium and that POM can be represented with the health benchmark value for B[a]P.

Figure 4. Cancer risks apportioned to source categories. This figure includes the assumption that POM can be represented with the health benchmark value for B[a]P.

Figure 5. Apportionment to individual pollutants of the upper-bound excess cancer risk to an average individual in Minnesota. This figure includes the assumptions that POM can be represented with the health benchmark value for B[a]P.
and selected metals. The statewide median concentration exceeded the health benchmark value for benzene, carbon tetrachloride, formaldehyde, and chromium. At specific individual monitoring sites, the median concentrations exceeded the health benchmark value for the additional pollutants chloroform, ethylene dibromide, and arsenic. It should be noted that the arsenic data as well as other metals data are questionable because of the large number of values below the LDL and the fact that the health benchmark values were often lower than the LDL. We can say with confidence that the monitoring data for at least five pollutants, and possibly as many as eight, exceed health benchmarks at one or more monitoring sites. Taken together with the modeling results, 11 pollutants exceed the health benchmark at one or more locations (Table 3). Despite the detection limit issues, we believe it is important to report these data, particularly the frequency with which we measured detectable values in relation to the LDL and the health benchmark values, as these data have implications for the planning of future monitoring efforts.

Figure 6 shows a box plot of concentrations of formaldehyde at each monitoring site. The 11 sites on the left side of the figure were located in the metro area, where generally higher concentrations were found. The median formaldehyde concentration exceeded the health benchmark value at all sites except one site in International Falls, where the median concentration was slightly below the health benchmark. The mean formaldehyde concentration exceeded the health benchmark value at all sites. This finding differs from the modeling results for formaldehyde, in which most of the sites outside the metro area were below the health benchmark value.

The cancer risks and noncancer hazard indices presented here apply to modeled and monitored concentrations in outdoor ambient air. Concentrations in indoor air and personal exposures are different from outdoor air concentrations. For many of the pollutants considered in this study the indoor air and personal air concentrations are often higher than outdoor air concentrations (11,12).

Comparison of modeling and monitoring. There was a tendency for the modeling results to underestimate when compared to measured values (Table 5). For 19 of 31 substances where model-monitor comparisons were possible, the mean percent difference (averaged over all monitoring sites) was within a factor of 2. For 8 substances the modeled values were higher, for 4 substances the model and monitor results were statistically equivalent, and for 19 substances the monitored values were higher.

Table 5. Comparison of modeled and monitored values.

| Substance                 | Monitored value (µg/m³) | Modeled value (µg/m³) | Percent difference a,b | Comparison |
|---------------------------|-------------------------|-----------------------|------------------------|------------|
| Vinylidene chloride       | 0.0855                  | 0.0000                | -100.0                 | M modeled values are higher |
| 1,3-Dichloropropene       | 0.0217                  | 0.0001                | -99.4                  |            |
| Hexachloro-1,3-butadiene  | 0.1989                  | 0.0018                | -99.0                  |            |
| Cadmium                   | 0.0022                  | 0.0002                | -91.8                  |            |
| 1,4-Dichlorobenzene       | 0.3206                  | 0.0568                | -86.3                  |            |
| 1,1,2-Trichloroethane     | 0.0274                  | 0.0025                | -82.3                  |            |
| Cobalt                    | 0.0007                  | 0.0001                | -77.7                  |            |
| Ethylene dibromide        | 0.0389                  | 0.0077                | -75.4                  |            |
| Arsenic                   | 0.0014                  | 0.0005                | -64.7                  |            |
| Acetaldehyde              | 1.0604                  | 0.4929                | -52.4                  |            |
| Propionaldehyde           | 0.1831                  | 0.1122                | -49.1                  |            |
| Ethylbenzene              | 0.6094                  | 0.3619                | -44.5                  |            |
| Manganese                 | 0.0065                  | 0.0035                | -40.0                  |            |
| Formaldehyde              | 1.6489                  | 1.0661                | -35.7                  |            |
| Styrene                   | 0.1085                  | 0.0881                | -20.0                  |            |
| Vinyl chloride            | 0.0061                  | 0.0026                | -12.5                  |            |
| Selenium                  | 0.0006                  | 0.0003                | -3.7                   |            |
| Chlorobenzene             | 0.0199                  | 0.0146                | -14.7                  |            |
| Chloroform                | 0.1526                  | 0.1070                | -27.1                  |            |
| Lead                      | 0.0043                  | 0.0035                | -8.3                   |            |
| Toluene                   | 3.1906                  | 3.2985                | -8.0                   |            |
| Chromium                  | 0.0010                  | 0.0017                | -7.0                   |            |
| Dichloromethane           | 0.4133                  | 0.3983                | -2.7                   |            |
| Benzene                   | 1.5349                  | 1.6860                | 12.9                   |            |
| Carbon tetrachloride      | 0.7890                  | 0.8882                | 14.3                   |            |
| Trichloroethylene         | 0.4732                  | 0.4752                | 0.43                   |            |
| Tetrachloroethylene       | 0.3835                  | 0.5063                | 21.8                   |            |
| Xylene                    | 2.4873                  | 2.9455                | 26.4                   |            |
| 1,3-Dichloropropene       | 0.0199                  | 0.0221                | 27.4                   |            |
| Dichloroethane            | 0.0389                  | 0.0627                | 102.0                  |            |
| Nickel                    | 0.0005                  | 0.0040                | 643.0                  |            |

The monitored values are calculated as the mean of the site means with each site mean covering the period of record for that site. The modeled values are calculated as the mean of the values for each census tract containing a monitoring site. For census tracts with more than one monitoring site, the tract is weighted by the number of monitoring sites. The percent difference is calculated as the mean percent difference averaged over all of the individual site/census tract comparisons. \(\frac{(\text{Model-monitor})/\text{monitor}}{\times 100}\).
Table 6 gives a comparison of the modeled and monitored values for cancer risks and noncancer hazard indices at each monitoring site. Estimated upper-bound cancer risk based on 16 monitored pollutants ranged from $4.7 \times 10^{-5}$ to $11.0 \times 10^{-5}$ based on 30 modeled pollutants the risk ranged from $3.9 \times 10^{-5}$ to $61.3 \times 10^{-5}$. The highest modeled cancer risk was $1.34 \times 10^{-2}$ and occurred in a census tract with no monitoring site. For 11 pollutants in common between the monitoring and modeling, the estimated upper-bound cancer risk ranged from $4.0 \times 10^{-5}$ to $10.3 \times 10^{-5}$ (monitoring) and $2.3 \times 10^{-5}$ to $8.0 \times 10^{-5}$ (modeling). The correlation coefficient between monitored and modeled risk with a common set of 11 pollutants (i.e., between columns four and five in Table 6) was 0.54, with the modeled risks higher at seven (all urban) of the 25 sites.

The noncancer hazard index at specific monitoring sites ranged from 0.6 to 2.0 based on 24 monitored substances, whereas the hazard index ranged from 0.6 to 26.9 based on 49 modeled substances. The highest modeled noncancer hazard index was 58.1 and occurred in a census tract with no monitoring site. For 15 pollutants in common between the monitoring and modeling, the index ranged from 0.6 to 1.9 (monitoring) and 0.2 to 1.2 (modeling). The correlation coefficient between monitored and modeled risk with a common set of 15 pollutants (i.e., between columns eight and nine in Table 6) was 0.36, with the modeled hazard index higher at only one of the 25 sites.

Trends. At some of the sites located in the metro area, monitoring data collection began in 1991, making it possible to look for trends toward increasing or decreasing concentrations during the period 1991–1998. M monitoring data sufficient to investigate the presence of a trend was available for eight of the pollutants of concern (arsenic, benzene, carbon tetrachloride, chloroform, chromium, ethylene dibromide, formaldehyde, and nick- el). We analyzed linear regressions over time (monitoring site). Of the pollutants considered here, a consistent trend across several monitoring sites. For the pollutants of highest concern, a consistent trend across several monitoring
sites was identified for only one, benzene, where concentrations decreased slightly but significantly. Further work is needed to evaluate possible trends for other pollutants.

Benzene concentrations have been measured since 1991 at the Minneapolis Public Library, Holman Field in St. Paul, and near Koch Refinery in Pine Bend. At each of these long-term monitoring sites, plots of the data over time showed that the measured concentrations appeared to have decreased slightly since the measurements were begun. A seasonal decomposition analysis was unable to show a significant seasonality in the benzene concentration; however, the values were generally slightly higher in winter than in summer (e.g., 1.82 µg/m³ in November through March vs. 1.57 µg/m³ for April through October at Koch site 420).

We performed linear regression analyses with the benzene data from each of the long-term monitoring sites. These analyses showed that the decrease in benzene concentrations over time were statistically significant (p < 0.05), although small. The linear regression coefficients (R² values) ranged from 0.02 to 0.03. The regression equations show that the benzene concentrations decreased by 0.02 µg/m³ per year (Koch 423) to 0.07 µg/m³ per year (Holman Field) to 0.11 µg/m³ per year (Minneapolis Library and Koch 420). Possible reasons for the slight decrease in benzene concentrations are uncertain. Over the period 1991–1998 the metro area vehicle fleet incorporated generally cleaner vehicles. In addition, a vehicle inspection and maintenance program was operative over that period. Finally, there were changes in fuel composition. Any or all of these factors, or some combination of them, may be involved in the trend toward lower benzene concentrations.

Formaldehyde concentrations have been measured since 1991 at the Minneapolis Public Library, Holman Field in St. Paul, and at Pine Bend (Koch sites 420, 423, and 426), and since 1993 at St. Paul Park. Plots of the data (e.g., Figure 7) appear to show that the measured concentrations increased over time. Figure 7 also shows that the data are seasonal, with maximum concentrations occurring in the summer and minimums in the winter. Figure 7 shows data from the Minneapolis Public Library site, but the data from this site are similar in terms of the seasonal and trend components to the other sites listed here.

Figure 7 appears to show an increase in formaldehyde concentrations over time, but it is important to understand whether there has indeed been an increase in formaldehyde concentrations, or whether the apparent increase can be attributed to other factors. Over the period of record, there have been at least two changes that could influence the formaldehyde levels. First, the measurement technique was changed to include ozone scrubbing in May 1995. Second, the amount of oxygenated fuel sold in the state increased from approximately 15% in 1991 to over 90% in 1998. There is speculation that increased use of oxygenated fuel may lead to higher emissions of certain pollutants such as formaldehyde.

To investigate the influence of these changes, we conducted a trend analysis on the formaldehyde data. First the data were deseasonalized. Next, two additional variables (in addition to the time, or trend, variable) were included in the analysis, one to account for the change in measurement technique and a second to account for the percentage of oxygenated fuel sold each month since 1991. Multiple linear regression showed that the only variable which was a statistically significant predictor of deseasonalized formaldehyde concentrations was the measurement technique. The variables for trend over time and percentage of oxygenated fuel were not significant. This finding was true for all sites. Thus we conclude that measured formaldehyde concentrations appear to have remained stable over time, and that the increased use of ethanol-containing fuel does not appear to have led to an increase in formaldehyde concentrations.

The importance of the change in carbonyl measurement technique by adding ozone scrubbing can be seen from Figure 7. The measurements were systematically lower in the time before ozone scrubbing. After May 1995, the measurements were not only systematically higher but also the seasonal component was much more apparent. The masking of the seasonal component in the nonozone-scrubbed data presumably occurred because ozone concentrations are typically higher in summertime, leading to greater formaldehyde destruction during the times when concentrations would otherwise be expected to be highest. As can be seen in Figure 7, the deseasonalized data (dotted line) still show some seasonality in the years 1995–1998. This occurs because the deseasonalization was done for the entire time series, including the data obtained before 1995, when the seasonality was masked. An alternative method would be to treat the data obtained from May 1995 onward separately.

Limitations. There are several important limitations to the work reported here, some of which have already been discussed. In summary we note the following:

- The set of pollutants considered was limited. Inclusion of additional pollutants would tend to increase estimated health risks.
- Only inhalation health impacts were considered. The inclusion of other exposure pathways would tend to increase estimated health risks.
- Because of the limited knowledge for the ambient air speciation of chromium, it is unknown to what extent the use of the hexavalent chromium health benchmark value may overstate the human health risk.
estimated for exposure to total chromium.

The toxicity value for B[a]P was used as a surrogate to represent the toxicity of PO M. This assumption may either over- or underestimate the actual toxicity of POM depending on the mix of substances that make up POM at a particular time and place; however, we believe that employing this assumption represents the actual risk better than using no value (i.e., assuming a zero risk for POM).

Metal analysis of PM10 filters by XRF was a marks. It appears that an alternative analytical technique is required to routinely detect metals on PM10 filters at sites like those in M. Innesota.

Modeled emission data were from 1990. Since 1990 there have been several changes that might alter the estimated estimates of pollutant concentrations. Methods for estimating emissions have improved over time. The improvements result in increases in reported emissions of some pollutants and decreases in others. In general, we expect emissions from point sources and several area source categories to have declined as sources came into compliance with the Natio nal Emissions Standards for Hazardous Air Pollutants (NESHAPS) (37). Some area source emissions are closely linked to population. Since population has increased in most places, emissions from these area source categories are likely to have increased. In the mobile source arena, both cars and fuels have gotten cleaner. On the other hand, vehicle miles traveled and fuel use have increased. We do not know the extent to which these counteracting trends offset one another.

The results pertain to outdoor air at specific stationary locations; however, people move from place to place and spend a large fraction of time indoors. In general, indoor concentrations of many of the pollutants reported here tend to be higher than outdoor concentrations, and personal concentrations tend to be higher still (11,12).

Three of the pollutants identified as major contributors to modeled cancer risks or noncancer hazard indices were not measured in this study: acrolein, 1,3-butadiene, and PO M. Future monitoring work should be undertaken to address these pollutants. A quantitative analysis of the uncertainties is not possible with the available information, but clearly some of the limitations lead toward errors of underestimating risks, whereas others lead toward overestimating risks.

Conclusion

We used modeling and monitoring to characterize air toxics concentrations in Minnesota. The estimated and measured pollutant concentrations were in turn used to evaluate health risks. Despite the shortcomings and the incompleteness of the available information, we believe the weight of evidence suggests that air toxics are an important public health concern in Minnesota, and that prudent and cost-effective measures for reducing emissions and air concentrations should be evaluated.

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