Human Exposure to Urban Air Pollution

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This study deals with some methods of making human exposure estimates, aimed at describing the human exposure for selected air pollutants in Sweden that are suspected carcinogens. Nitrogen oxides (NO_x) have been chosen as an indicator substance for estimating the concentration of the urban plume. Earlier investigations have shown that the traffic in Swedish cities contributes around 85% to the measured NO_x concentrations, and that most of the mutagenicity in urban air originates from traffic. The first section of this paper describes measurements in Stockholm of some unregulated light hydrocarbons, such as ethene, ethyne, propane, propene, butane, and isobutane. In addition, measurements of some volatile aromatic hydrocarbons are presented. Simultaneous measurements of carbon monoxide (CO) were made. The ratios between CO and the individual specific compounds were determined by linear regression analysis. By analysis of relationships between CO and NO_x, NO_x concentrations can be used as a tracer to describe the exposure for these specific compounds. NO_x are considered to be a better tracer than CO, because NO_x or NO_2 values exist for many places over a long time, while CO is measured mostly in streets with high concentrations. At low concentrations, instruments that measure normal CO levels give no detectable signals. Through use of atmospheric dispersion models and models that describe how people live and work in urban areas it has been possible to describe the average exposure to NO_x in cities of different sizes. The exposure to NO_x for people living in the countryside has also been estimated. In this way, it has been possible to calculate the average exposure dose for NO_x for the Swedish population. This figure is 23 $\mu g/m^3$. By use of the relationships between NO_x and specific compounds the average dose has been calculated for the following compounds: polyaromatic compounds (PAH); ethene, propene, and butadiene; benzene, toluene, and xylene; formaldehyde and actaldehyde; nickel, chromium (VI), arsenic, and cadmium; asbestos; and silicon. — Environ Health Perspect 102(Suppl 4):39–47 (1994).

Key words: carbon monoxide, nitrogen oxides, polyaromatic compounds, urban air pollution

Introduction

Human exposure to urban air pollution can in principle be estimated in three ways: *a*) the concentration of hazardous substances in the urban air in different environments can be recorded or modeled together with movements of individuals or population groups; *b*) personal samplers can be used; and *c*) the target dose in man can be determined, e.g., blood.

Determining human exposure is a very complex task, and most attempts to estimate it in risk assessment articles rely on literature data on normal pollutant concentration. This probably results in overestimations of average exposures, since measurements are made mostly in areas where there is a reason to survey the air quality. The study reported here also uses commonly available data and makes corrections for such biases.

The steps from emission to human exposure consist of source emissions, transport and transformation, accumulation in the environ-

ment (indirect uptake via food), and human exposure.

A complex task is the measurement of volatile organic compounds and polyaromatic compounds in urban air, the latter both in the gas phase and the solid phase. These analyses are expensive and therefore are made to a limited extent. However, if major air pollutants, such as CO and nitrogen oxides (NO_x) are measured in a more continuous way, and these specific pollutants are measured during a limited time, it is possible to get quotas between NO_x and specific pollutants like ethene.

In this estimate, the exposure of the Swedish population to NO_x and carcinogens in urban air has been calculated using NO_x as an indicator substance. The results will form the basis of cancer risk assessment.

Air Quality Data

Air quality data in Sweden are known from point measurements and from dispersion modeling of more or less well known emissions. Measured data exist for sulfur dioxide, soot (black smoke), and nitrogen oxides in air, but data on the genotoxic substances in which we are interested are rare. It is still possible to estimate the concentrations of the genotoxic components by assuming that the

ratios between the substances are nearly constant. This is not unreasonable, considering the relatively large contribution from car traffic and the moderate dispersion time and room scales involved. The ratio between different components in car exhausts is not likely to change notably during its residence time in the city air (about one hr). Most atmospheric reactions are too slow to alter the ratio more than marginally.

Despite the negative correlation between black smoke and NO_x during a drive cycle of an individual car, the mixed pollution from many cars being run at various conditions may still show a positive correlation between black smoke and NO_x (1).

If we thus have determined the mean exposure of the population to NO_x, we can calculate the mean exposure of the population to another component by simply multiplying the NO_x value with the mean ratio between the component and NO_x. The reason for selecting NO_x as a tracer for genotoxic substances is that some 80 to 90% of the NO_x in urban air is generated from traffic and that most of the NO_x and genotoxic substances in urban air originate from sources within the own urban complex. For other substances, such as SO_2, a large part may originate from long-range transport.

The concentration of NO_x in urban areas is seldom measured in small- and medium-sized cities. Only in a few of the larger cities are there data series from longer periods. However, in about 60 Swedish cities, the winter mean of NO_2 has been determined in the city centers over a 5-year period using a sodium arsenite method (2), and on five regional background stations as winter and yearly means (3). The NO_2 concentrations correlate somewhat to the number of inhabitants.

Light Hydrocarbons and Other Volatile Organic Compounds

Results presented here are an extended summary from a report by Persson and Almén published by the Swedish Environmental Protection Agency (2). Measurements were made of ethene, ethyne, propane, propene, butane, and isobutane in the air of central Stockholm. A statistical presentation was carried out simultaneously with data for CO. Special emphasis was given to the determination of the source contribution from vehicle traffic to the various compounds. The sampling program, covering the period from December 1986 to August 1987, was coordinated with the Stockholm Municipal and Environmental Health Administration (SMEHA) program for air quality supervision. The measurements were made from a mobile air quality monitoring station, belonging to SMEHA. However, the measuring program, sampling, and analysis are described in detail elsewhere (2).

Results and Discussion

Our results are based on 1-hr mean values. The investigation shows that the heavy traffic sites had an increased concentration of all hydrocarbons, compared to the low traffic sites, i.e., 5 to 10 times. Markedly higher levels of the unsaturated hydrocarbons, ethene, ethyne, and propene were found here, compared with the saturated compounds. The contribution of traffic to various hydrocarbons was investigated using CO as an indicator substance for the traffic.

The average values for the measured unsaturated compounds in the heavy traffic sites were in the magnitude of 10 to 20 ppb, and for the saturated compounds 1 to 10 ppb. A strong correlation indicates origin from the same source. Strongest correlation (r) was found at the high-traffic sites, the unsaturated HC having stronger correlation than the saturated HC. Propane was the only HC in which the regression equation had a significant positive intercept, i.e., a positive concentration at zero CO. This indicates that propane occurs in the background air of Stockholm. The intercept was highest during the winter, lower in spring, and not significant
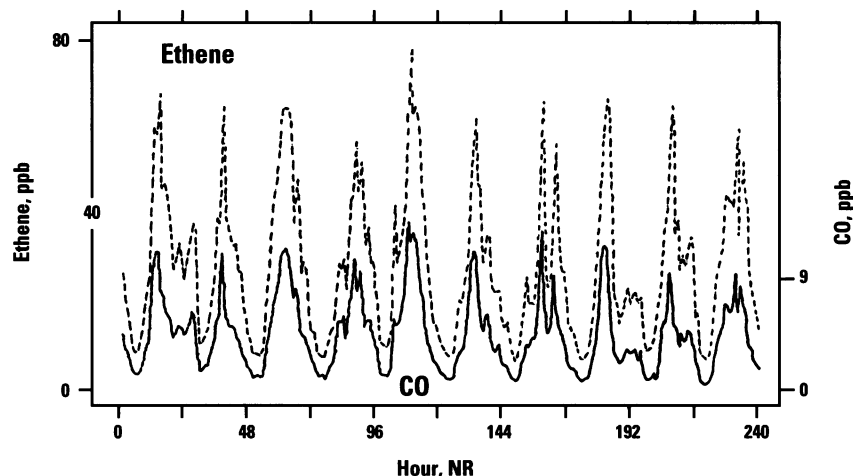

Figure 1. One hour time sequence for the concentration of ethene and CO at Sveavägen from 29 November to December 1986.

Table 1. Average concentrations and ranges for D, T, C, and B series.

Component	Unit	+Location Average	+Location Range	−Location Average	−Location Range
C series, 10 periods					
TSP	$\mu g/m^3$	58	22–200	46	16–160
Soot	$\mu g/m^3$	17	3.5–48	17	2.3–48
Lead	ng/m^3	160	12–640	140	27–400
Mutagen TA98–S9	rev/m^3	11	1.3–47	9.6	1–38
Mutagen TA98+S9	rev/m^3	8.4	0.8–34	8.7	0.6–37
-PAH	ng/m^3	9.7	0.6–42	9.9	1.2–33
1-Nitropyrene	pg/m^3	8.6	<1–36	3.8	<1–11
Benzene	$\mu g/m^3$	3.4	<0.3–7.9	2.9	0.3–7.0
D series, 12 periods					
TSP	$\mu g/m^3$	140	29–350	86	33–190
Soot	$\mu g/m^3$	59	6.6–190	26	7.3–43
Lead	ng/m^3	730	49–1900	700	110–1600
Mutagen TA98–S9	rev/m^3	13	1.1–35	12	2–30
Mutagen TA98+S9	rev/m^3	13	1.4–39	12	2–28
-PAH	ng/m^3	24	1–57	17	2.8–38
1-Nitropyrene	pg/m^3	20	1–68	12	2–35
Benzene	$\mu g/m^3$	17	0.7–50	14	4.2–26
T series, 16 periods					
TSP	$\mu g/m^3$	74	20–280	51	15–200
Soot	$\mu g/m^3$	28	7.6–70	17	5.4–55
Lead	ng/m^3	250	60–930	140	21–380
Mutagen TA98–S9	rev/m^3	8.3	2.1–18	6.3	0.5–18
Mutagen TA98+S9	rev/m^3	8.5	2–16	6.2	0.3–19
-PAH	ng/m^3	18	3.3–57	9.5	0.7–33
1-Nitropyrene	pg/m^3	14	1–42	6.8	<1–32
Benzene	$\mu g/m^3$	9.6	1–30	6.7	0.3–24
B series, 5 periods					
TSP	$\mu g/m^3$	140	40–230	66	28–120
Soot	$\mu g/m^3$	47	14–88	29	2.7–59
Lead	ng/m^3	380	200–700	170	33–300
Mutagen TA98–S9	rev/m^3	11	5.2–16	7.3	2.9–13
Mutagen TA98+S9	rev/m^3	15	4.8–22	7.3	2.1–15
-PAH	ng/m^3	38	8.8–79	14	2.9–25
1-Nitropyrene	pg/m^3	17	6–32	12	3–24
BNT	ng/m^3	0.59	0.06–1.2	0.16	0.06–0.27
Benzene	$\mu g/m^3$	12	6.3–17	6.7	4.2–11

Abbreviations: C, central (C+) and noncentral (C−); D, high-diesel (D+) and low-diesel (D−) location; T, high-traffic (T+) and low-traffic (T−) flow location; rev, revertant.

in the summer. The lower intercept during the warmer period of the year may reflect the higher rate of photochemical degradation and a better air mixture than in the winter. The divergent observations of HC were found in the time series by study of the difference between the actual value and the value given by the regression equation, with CO as input data. In this way, the observations could be extracted from vehicular influence. At sites near dense traffic, all HC showed a strong correlation to CO, which can be assigned solely to the vehicle traffic. The good covariance in time, hour for hour, is exemplified in Figure 1 with ethene and CO over 10 days.

Polycyclic Aromatic Compounds

Among the several thousand compounds present in ambient air are the polycyclic aromatic compounds (PAC), of which some are known carcinogens and suspected mutagens (*3*). The most important sources in Swedish cities are mobile—light- and heavy-duty vehicles emitting exhaust containing PAC. Results presented below emanate from samples collected at several locations in the Gothenburg urban area. Sampling, chemical analysis, and results are presented in detail in a report published in Agurell et al. (*1*). The results from Gothenburg are from areas with traffic densities denoted as central (C+) and noncentral (C−) locations, high-diesel (D+) and low-diesel (D−) locations, and high-traffic (T+) and low-traffic (T−) flow locations. In Table 1 average concentrations and range are presented. From the table it can be seen that the concentration of polycyclic aromatic hydrocarbons (denoted as "Sum PAH," the sum of 14 selected individual PAHs, such as phenantrene, antracene, fluorantene, pyrene, benzo[*g,h,i*]fluoranthene, cyclopenta[*cd*]pyrene, benz[*a*]antracene, chrysene/ triphenylene, benzo[*e*]pyrene, benzo[*a*]pyrene, indenopyrene, benzo[*g,h,i*]perylene, and coronene) are approximately 20 ng/m^3. Corresponding values for 1-nitropyrene are approximately 10 pg/m^3.

The T-sampling series (high-traffic-flow location) was measured for 18 months with a time resolution of 1 month. In Figure 2, the variation of PAH concentrations is presented, from which it can be seen that during the winter an increased PAH concentration can be measured a factor of approximately three to five times that of the summer. A possible explanation for the increase is that during winter automobile engines are running on richer fuel-air mixtures, and contributions are coming from domestic heating and meteorologic conditions.

In addition to PAH measurements, 1-nitropyrene also was measured; it showed a larger variation than PAH (Figure 2), indi-
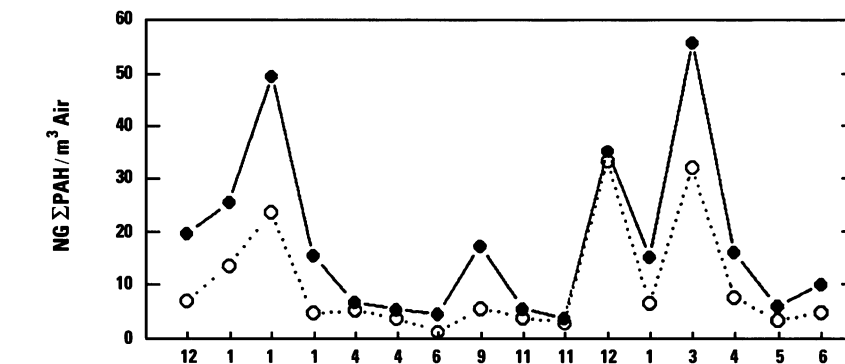

Figure 2. The variation of the PAH concentration over 1.5 years within the T+ (●) and T- (○) series.

cating a significant impact from atmospheric transformation on measured 1-nitropyrene concentrations.

Summary

A seasonal variation of a factor three to five has been determined for the PAH concentration in Gothenburg ambient air samples, i.e., winter/ summer. Average concentration determined in Gothenburg ambient air for PAH was 20 ng/m^3, 1-nitropyrene 10 ng/m^3.

In central Stockholm, the vehicle traffic is an important source of some light non-methane hydrocarbons (LNMHC). The investigation shows that carbon monoxide can be used as a tracer in the urban air for LNMHC originating from vehicle traffic. The quantitative relationship between CO and individual HC was rather stable for unsaturated HC, independent of traffic intensity and time of year. Saturated HC showed greater seasonal variations.

From this investigation we learned that a simple way to grasp the pollution pattern from traffic is to study intensively the pollutants directly near dense traffic during a few days and nights. The time resolution should be at least one hr, to detect, among other factors, the rush hours.

The covariance in time between different compounds gives valuable information on the stability of the pollution pattern and also on the occurrence at other sources than traffic. If CO is selected as tracer for traffic, the quantitative relationship toward the individual compound is made by linear regression analysis. Exposure doses for citizens to the different components can then be made indirectly with the use of representative data for CO doses.

Method of Estimating Human Exposure

An overview of methods used today to estimate human exposure to air contaminants was

made by Omstedt and Szego (*6*). In most cases, except when directly measuring the biologic dose, the methods are based on the identification of a number of microenvironments, with similar exposure conditions occurring within each microenvironment. The total dose is calculated on the basis of how long people stay in different microenvironments. An example of time-activity patterns in the western world is shown in Table 2.

Exposure data are estimated by the use of measurements and/ or models. Measurements are done either by exposure measurements or by measurement of the biologic dose. Exposure measurements may be done by personal monitors or by stationary monitors. In the latter case, one has to know the activity patterns of the population studied.

The models used can be divided into three classes: physical, statistical, and physical–statistical. The borders between these classes are not clear and the classification is based more on typical conditions than on the absence or presence of physical or statistical elements in the models. In our study, we have used a physical–statistical model together with air quality data from stationary sources. The mean exposure in a city is determined from the expression:

Table 2. Time-activity patterns in the Western world.

Place	Number of hours on each place	
	Chapin (*30*)	Szalai (*31*)
Indoor		
At home	16.03	16.75
At work	4.61	4.03
Other things	1.31	1.63
Outdoor		
At home	0.27	0.23
Other things	0.27	0.12
Traveling, all types	1.16	1.25
Total	23.65	24.01

$$C = K_1 \times K_2 \times K_3 \times K_4 \times C(NO_2) \qquad [1]$$

where K_1 is the ratio of the mutagenic substance and NO_x; K_2 is the ratio of winter and year means; K_3 is the ratio of population exposure mean and central city mean; K_4 is the ratio of NO_x and NO_2.

The NO_x concentration is thus chosen as a tracer for the general pollution level in the urban plume. The reason for this is explained in the section, "Air Quality Data," but it may also be expressed as an attempt to decrease the overall error in estimation of the average exposure using available data. The correlation between the various parameters mentioned in the formula above may be low, but the precision in estimating the mean ratio (K_1 to K_4) increases considerably with the number of observations available.

One may also regard the method of estimating average exposure as a method of estimating a correction factor that transforms the average concentration from a limited number of measurements of a substance to the grand population average. This correction factor is the ratio between the grand average of population NO_x exposure and the average of NO_x measured parallel to the substance average.
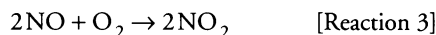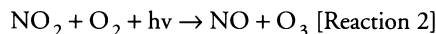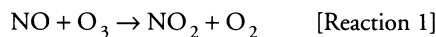
When estimating risks that are linearly dependent on exposure and when estimating risks for large groups, the individual exposures do not have to be determined. This means that the population exposure can be determined by multiplying the number of people in a certain microenvironment by the time period and the concentration, and successively adding all such exposure data from different microenvironments to get the total exposure in a city or part of the country, without knowing how people move between the different microenvironments.

Each city or rural part of the country is regarded as a microenvironment. For the two largest cities, Stockholm and Gothenburg, transportation is also considered a microenvironment. Each city with an urban population more than 20,000 is treated individually, while urban communities with a population less than 20,000 are treated in groups of 20,000 to 10,000, 10,000 to 5,000, 5,000 to 1,000, and 1,000 to 200, respectively.

An urban area is not an ideal microenvironment since the concentration varies within the area, a circumstance that has not been possible to consider in detail except for the city centers. For the rest we have introduced a correction factor for the concentration measured or estimated for the central parts. The correction factor is the ratio between population-weighted mean concentration and central concentration. This factor has been deter-

mined by Svanberg et al. for Gothenburg (7), and by Lövblad et al. for Helsingborg and Örebro (8). The correction factor was 0.56 for Gothenburg for only its own air pollution, and 0.68 for the regional background. For Helsingborg the correction factor was 0.43, and for Örebro 0.61 regarding the cities own pollution. A population-weighted mean for these cities would thus be 0.55 for each cities' own air pollution, and 0.7 including the regional background. The regional background for Helsingborg and Örebro has been assumed to be the same as the mean background in Sweden, which is about 20% (2).

To find out the NO_x concentration corresponding to the measured NO_2 concentration, one has to consider the atmospheric chemistry of NO_x. The most important reactions are:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad [\text{Reaction 1}]$$

$$NO_2 + O_2 + h\nu \rightarrow NO + O_3 \qquad [\text{Reaction 2}]$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad [\text{Reaction 3}]$$

A large number of other reactions occur, especially with hydrocarbons, but their influence on the mean ratio between NO_2 and NO_x is considered small during the first hour after its emission into the average Swedish urban atmosphere. Reactions 1 and 2 are fast. After a few minutes there is a chemical equilibrium (where k_1 and J are rate constants for reactions 1 and 2), which can be expressed as:

$$(NO_2) = \frac{k_1}{J(NO)(O_3)} \qquad [\text{Reaction 4}]$$

From this expression (NO) can be determined if we know (NO_2), (O_3), k_1 and J.

Photochemical equilibrium can approximately be expected to occur in rural areas. In urban areas, however, the time necessary to mix NO-rich air with background, ozone-rich air is also important.

Reaction 3 is dependent on square of the concentration of NO and is most important where the concentration is high, i.e., close to the source. Besides the reactions above, there is a certain primary production of NO_2 in the source in the order of a few percent. With a simple box-model including atmospheric chemistry and mixing processes designed by Hertel and Bercowics (9), Omstedt has calculated the NO_2 concentration as a function of the NO_x concentration (10). Regional background concentrations were taken from Dahlberg et al. (10) and Larsen (11), and sun radiation data were taken from the Swedish Metorological and Hydrological Institute (12); 5% of the NO_x have been assumed to exist as NO_2 at the point of emission. The result is shown in Figure 3.

Figure 3 shows two curves. The lower represents photochemical equilibrium. In the higher, mixing time in urban areas has been considered. The points are measured data by a chemiluminescent method from central Gothenburg during 1985. The measurements were carried out at roof-level. When calculating NO_x values from NO_2 values in urban areas, the NO_2 concentration is multiplied by a factor of 2.5. In rural areas, this factor is assumed to be 1.1.

Since most of the NO_2 data were measured during the winter, it is necessary to know the ratio between the yearly mean and the winter mean. In Gothenburg this ratio is 0.6, and this ratio is used for the other cities until further statistics exist. For the rural areas, measured data represent the entire year (3).
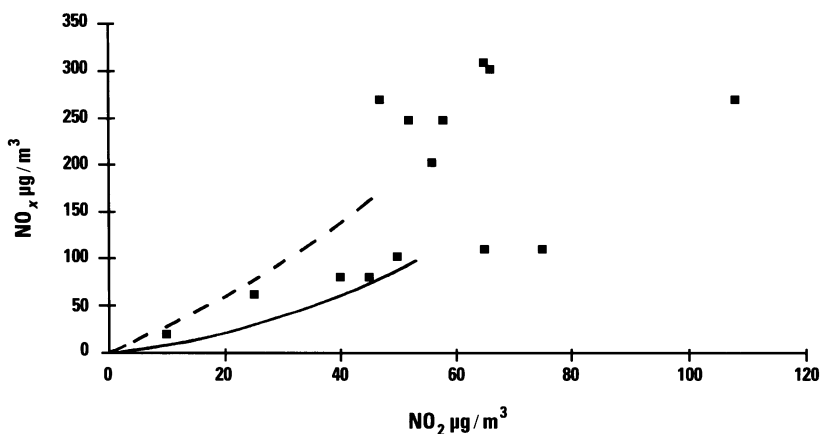

Figure 3. Modeled and measured NO_2 concentration as a function of the NO_x concentration.

The fact that people spend most of their time indoors must also be considered. No systematic determination of this factor has been made for Sweden, but measurements in United States show indoor/outdoor ratios of about 0.8 for lead (*27*). This indicates that a factor of one may be used as a first approximation for most inert substances. However, substances that occur in large particles (in this case silicon) are given a factor of 0.5, representing its penetration into buildings.

As described above, population exposure to NO_x can be determined for the general ambient air conditions in urban and rural areas. However, as shown in Table 2, much time is spent in the transportation system, where the concentrations usually are considerably higher. Further there is a greater number of travelers when the concentrations peak in the morning and afternoon. The contribution to the population exposure dose may be written (where K is a constant that represents the mean ratio between NO_x concentration and traffic flow, or number of vehicles per day):

$$\frac{K \times n_k 2 \times 1_k}{V_k} \quad [2]$$

This ratio has been measured during a 2-week period on 20 streets in Gothenburg. The mean value of K was estimated to 0.04 µg NO_x/m^3/vehicle/day during peak traffic hours. Earlier estimates from NO_x concentration measured at the roadside indicate K values of 0.004 µg NO_x/m^3 per vehicle/day, with NO_x values as daily means (*7*). The figures are approximately in agreement, assuming that the number of vehicles in the peak hours is about 10% of the number per day.

Through assistance by the local community planning office, the expression illustrated above was used on all major streets in Gothenburg to calculate the exposure dose to the travelers (*5*). The exposure was calculated for peak hours, and the rest of the day was divided in work hours, evening hours, and night hours.

For Stockholm, the exposure was estimated by the use of figures from a Stockholm country council investigation of traveling habits during 1990. According to these data, the mean traveling time in cars to work and back is 440,000 hr/day. There are no measurements of the mean concentrations within the cars, but there is no reason to assume a lower concentration than in Gothenburg. The concentrations have thus been assumed to be 0.7 µg/m³ as a mean. The ratio between the exposure-dose from traveling to and from
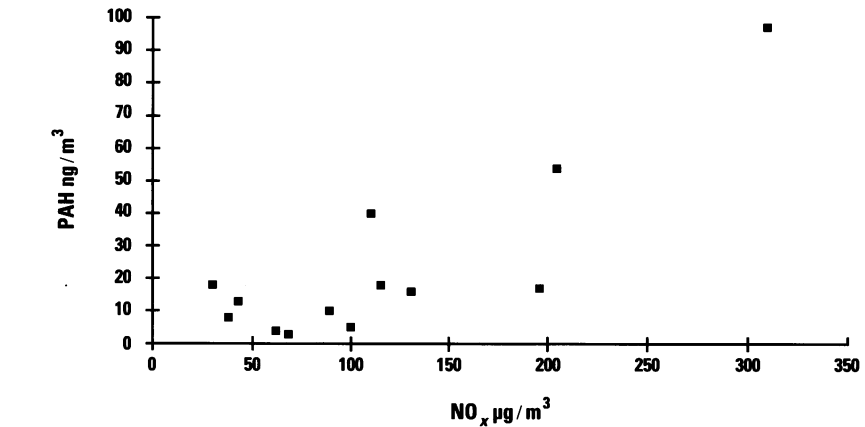

Figure 4. Nitric oxide (NO_x) and PAH concentrations in central Gothenburg.

work during peak hours and from all traveling in the traffic system during the day was 0.27 in Gothenburg. This is also assumed to be the case in Stockholm.

The exposure-dose in other cities has been neglected. This is thought to introduce only a minor error to the overall exposure estimate since the dose is proportional to the square of the traffic intensity and since the traveling time is much higher in large cities than in small- and medium-sized ones.

The method we have used to calculate the mean exposure thus starts with measurements of winter mean concentration of NO_2 in the central parts of 60 Swedish cities, and estimating the concentration in the remaining cities by regression analysis. Then the population-weighted mean exposure of NO_x is determined for each city by multiplying with a number of correction factors. Finally, a population-weighted mean for all the country is calculated for NO_x and this value is multiplied with various factors expressing the mean ratio between different mutagenic substances and NO_x to give the mean exposure to these substances.

Calculations and Results

Mean Exposure to NO_x

The number of inhabitants, the winter mean of NO_x, the corrected population mean

exposure of NO_x and the total population exposure for each city larger than 20,000 inhabitants and for groups of communities with less than 20,000 inhabitants has been calculated by Steen (*12*). The corresponding figures are also given for rural areas. The exposure of 21 µg/m³ is obtained. If the travelers' exposure-dose in Stockholm and Gothenburg (12 and 5 person/year/g/m³) is added, the mean exposure increases to 23 µg/m³.

Mean Exposure to PAH. The PAH/NO_x ratio in Gothenburg may be determined to approximately 0.2 × 10⁻³ on the basis of data from Brorström et al. (*13*) and Agurell et al. (*1*) (Figure 4). The PAH/NO_x ratio in car exhausts may be calculated for the fleet in central Gothenburg around 1985 to 0.1 × 10⁻³. The figures used for the calculation are given in Table 3.

Since the population mean exposure for NO_x is 23 µg/m³, the corresponding mean PAH exposure was 0.2 × 10⁻³ × 23 µg/m³, which is 4.6 ng/m³. This is exposure in traffic-dominated areas. In most small cities and villages the concentration of black smoke is higher compared to the NO_x concentration, probably because of an increased use of small-scale burning of oil and wood, which also generates some extra PAHs. The ratio of winter means of locally generated concentrations of black smoke and NO_x correlate nega-

Table 3. Emission factors and traffic data used for calculating mean ratio of PAH to NO_x and ethene to NO_x in central Gothenburg. [a]

Type of vehicle	Traffic work 1985, %	Emission factors		
		PAH, µg/km	Ethene mg/km	NO_x, g/km
Gasoline car	86	150	85	2.6
Gasoline car, cat	0	4	8	0.5
Diesel car	8	700	60	1.0
Diesel truck	4	4800	230	15

[a] For further information refer to Steen (*12*).

Table 4. Emission factors of PAH and inorganic carbon from various sources (14).

	PAH, mg/kg	Inorganic carbon, mg/kg
Gasoline cars	1.5–5	30–60
Diesel trucks	8	3000
Small-scale wood burning	40	2000
Small-scale oil burning, light oil	1	150
Medium- and large-scale burning of heavy oil	0.02	750

Table 5. Final use of energy in Sweden (29).

Final use for energy purposes	Industry	Transportation	Other
Coal, ktons	890	0	71
Coke, ktons	935	0	3
Wood, liquors, waste, peat, kton toe	3724	0	970
Small-scale wood firing			3560 tons (29)
Gasoline, 1000 m³		5908	
Light oils, 1000 m³		1045	13
Diesel oil, 1000 m³	28	2215	686
Fuel oil no. 1, 1000 m³	446	80	2962
Fuel oil no. 2–5, 1000 m³	1362	100	485
District heating, toe	~360		~2600
Electric heating, toe	~4900	~220	~5700

tively with the number of inhabitants in the different cities (2).

There are not enough data, however, to determine this exposure in a direct way. Since we can expect that the contribution from wood burning is significant, an attempt will be made to estimate it from the increased black-smoke concentrations and estimation of the black-smoke/PAH ratio. Black smoke is measured and defined by an Organization for Economic Cooperation and Development (OECD) method (28).

According to Larssen, the PAH emission and inorganic or elemental carbon emissions are as listed in Table 4 (14) (elemental carbon is the main constituent in black smoke). The concentration of black smoke compared to NO_x is about twice the relative concentration in Gothenburg. If the extra black smoke were to come only from small-scale wood burning it would contain: $(40/2,000)/((8 \times 0.32 + 2 \times 0.68)/(30,000 \times 0.32 + 50 \times 0.68) = 5.1$ times as much PAH per black-smoke unit as in Gothenburg. Of the total fuel consumption for transportation, the use of diesel was 32% and gasoline 68%. If the extra black smoke were to come only from small-scale burning of light oil, the increase would be 1.7 times and for heavy oil in large incinerators 0.0005 times as much.

To weight these figures together, the fuel consumption in Sweden during 1989 is used (Table 5). Emissions from heavy oil are assumed not to influence the ratio because of the dispersion from large stacks. The weighted mean value is estimated to about four.

Thus, we would need to add $4 \times 0.2 \times 10^{-3} \times$ exposure-dose for 6 million inhabi-

tants living in small- and medium-sized cities. This corresponds to an increase to the overall mean exposure of 14.2 $\mu g/m^3$, which will give a total exposure of 19 $\mu g/m^3$. The mean PAH composition in Gothenburg was: a) phenantrene, 5.5 weight %; b) anthracene, 0.4 weight %; c) fluoranthene, 11.5 weight %; d) pyrene, 10.5 weight %; e) benzo[a]pyrene, 3.5 weight %; f) benz[a]anthracene weight %; g) dibens[a,h]anthracene, <2 weight %; and h) benzo[b,j,k]fluoranthene, 0.5 wt %.

Mean Exposure to Ethene. The mass concentration ratio ethene/CO has been determined by Persson and Almén in Stockholm at Sveavägen to 5.7×10^{-3} and at Hornsgatan to 6.1×10^{-3}, and to 8.6×10^{-3} and 14.9×10^{-3} in car exhausts (2). Another test on a gasoline-powered car (15) shows a ratio of 12×10^{-3}. The ratio of CO/NO_x concentrations has been determined in Gothenburg to be 11.2 (16). This will give an ethene/NO_x ratio of 6.6 × 10^{-2} using the mean values from Hornsgatan and Sveavägen. The ratio ethene/NO_x in the urban plume from Gothenburg may be found from measurements made outside Gothenburg by Lindskog (17). It was the 6.3×10^{-2}. The ethene/NO_x ratio in car exhausts is 3×10^{-2} using the data shown in Table 3.

Using the mean value for the ratios found in ambient air, the mean population exposure may be determined to be 1.5 $\mu g/m^3$. However, this figure does not include contributions from woodburning. If we use the same type of reasoning as for PAH and use the ratio of ethene/PAH in emissions from small-scale burning of wood (about 23) there

will be an additional ethene concentration of 0.3 $\mu g/m^3$ to the mean exposure concentration, i.e., totally 1.8 $\mu g/m^3$.

This population mean exposure concentration may seem low if compared with earlier estimates made in Canada by the National Research Council of Canada (NRCC) (18). NRCC has made an extensive literature study and reports concentrations between 0.5 and 8000 $\mu g/m^3$. In a report from Reid and Watson (19), values of 14 $\mu g/m^3$ are claimed to be typical for forest and agricultural areas outside Calgary, Alberta, in Canada. In Sweden, we find only some tenth of a microgram at Rörvik, outside Gothenburg.

Some of these discrepancies may be explained by the skewed selection of data that comes out of a literature study. For different reasons, it is more interesting to make studies during circumstances with high concentrations than with low or normal ones. But it cannot be excluded that there is a significant difference in ethylene exposure between Canada and Sweden, or eventually North America and Europe.

We can impose two types of quality control on our data. The first is to compare measurements from different laboratories. As mentioned above, the ethene/NO_x ratio determined by different laboratories differed only slightly (5%). The second involves comparing the ratios with emissions ratios. Even if there is some difference, the data of the ratio in emissions are of the same order of magnitude and the maximum deviation is a factor of two. The ethene data obtained at Rörvik have been further obtained and reported within the European TOR project, where they have been accepted as reasonable.

Mean Exposure to Propene. The concentration of propene in Stockholm is about one-third that of ethene, according to Persson (2). This gives a mean exposure of 0.5 $\mu g/m^3$. A few measurements from burning of wood indicate a six-fold propene emission compared to ethene, which would give a contribution to the mean exposure of 1.8 $\mu g/m^3$. The total propene exposure would thus be 2.3 $\mu g/m^3$.

Mean Exposure to Benzene, Toluene, and Xylene. Most of the benzene, toluene, and xylene in urban air originates from traffic; but local contributions from the oil industry, wood burning, and solvent use may also contribute. The ratio between the mass concentrations of benzene and CO measured in Stockholm was 0.0142. Using normal CO/NO_x ratios a benzene/NO_x ratio of 0.16 may be found, corresponding to an average benzene exposure of 3.7 $\mu g/m^3$. The concentrations of toluene and xylene in Sweden are normally two to three times as high as the benzene concentration. During

our measurements in Gothenburg, the ratio to benzene was 3.4 and 4.0, which is higher than normal. The ratio 3 is used here for the entire country, giving the mean exposure to 11 $\mu g/m^3$ both for xylenes (o, m, and p) and toluene.

Mean Exposure to Formaldehyde. The concentration of formaldehyde at Hornsgatan in Stockholm is 0.77 ppb/ppm CO according to Persson and Almén (2). Using the ratio between CO and NO_x we obtain a formaldehyde/NO_x ratio of 0.009. The mean exposure of primary formaldehyde will therefore be 0.2 $\mu g/m^3$. Because formaldehyde also is a secondary pollutant through photochemical reactions, the total exposure should be somewhat higher. A few measurements outside Gothenburg at Rörvik indicate concentrations in the order of 1 $\mu g/m^3$ (23). According to Shah and Singh (20), the mean is determined by a few episodes and is about twice as high as the median values. The mean value at Rörvik is therefore estimated to be about 2 $\mu g/m^3$. Further, Rörvik has about double the concentrations of regional background as the demographic mean of Sweden, where the overall mean of the population exposure is estimated to be 1.2 $\mu g/m^3$.

Mean Exposure to Acetic Aldehyde. During measurements made in Sweden the concentrations of acetic aldehyde have been on the level of or somewhat lower than that of formaldehyde (21). Shan and Singh report concentrations that give a ratio between acetic and formaldehyde of 0.9 on weight basis (20). This means that the mean exposure in Sweden should be about 1 $\mu g/m^3$. The use of ethanol in car fuel has given an acetic aldehyde concentration above that of formaldehyde in Brazil (22).

Mean Exposure to Nickel. A mean Ni concentration of 5 ng/m^3 was measured in central Örebro (23). The concentration of NO_x was then about 50 $\mu g/m^3$. The ratio Ni/NO_x was then 0.1×10^{-3} and the mean exposure will be 2.3 ng/m^3. Measurements in Almhult (8,000 inhabitants, middle of southern Sweden) show concentrations of this order of magnitude (24).

Mean Exposure to Hexavalent Chromium. A mean Cr concentration of 7 ng/m^3 was found in Örebro during the same measurements referred to in "Mean Exposure to Nickel." This corresponds to a mean exposure of 3 ng/m^3. The percentage of the Cr that is hexavalent is not known. The only information we have is that hexavalent chromium was 10% of the total in a smelter's plume during measurements made 15 years ago. If we assume that most of the Cr in normal air is in mineral particles and only a small portion is water-soluble, perhaps 1% of the

Cr may be assumed to be hexavalent until further information is available. The mean exposure of hexavalent Cr is therefore estimated to be 0.3 ng/m^3.

Mean Exposure to Arsenic. At the measurement in Örebro mentioned above, the mean concentration of As was 6 ng/m^3, indicating a mean exposure of 2.8 ng/m^3. During our measurements in Gothenburg, we found an As/benzene ratio of 3×10^{-3}. With the benzene/NO_x ratio earlier determined at 0.16, we obtained an As/NO_x ratio of 0.5×10^{-3}, which in turn indicates a mean exposure of 11 ng/m^3. The mean value 7 ng/m^3 is used as an estimate for the whole population.

Mean Exposure to Cadmium. The mean concentration of Cd in Örebro was 0.65 ng/m^3 during the same measurements as above, indicating an overall mean exposure of 0.2 ng/m^3.

Mean Exposure to Asbestos. The only measurement known to us in Sweden of asbestos in ambient air was made in Stockholm in 1981. It showed that the number of fibers detectable with an optical microscope was 3,000/m^3 or lower. If the analysis was made in an electronic microscope, the number was 9,000 to 10,000 fibers/m^3. Considering the relatively high NO_x concentrations in Stockholm compared to the mean exposure concentration, the mean exposure concentration of asbestos fibers is estimated to be 200 optically detectable fibers/m^3 and 5,000 electro-microscopically detectable fibers/m^3.

Mean Exposure to Silicon. The concentration of silicon (Si) was measured within this project by energidispersive X-ray fluorescence on samples collected on membrane filters. The mean mass fraction of Si in the particles was 9%. The air sample inlet was an inverted funnel giving an approximate cutoff at 10 to 20 μm, thus collecting inhalable particles (IP). The ratio IP/TSP (total

suspended particles) was determined to be 0.65 as an average in an American study (25). In our study, the TSP/benzene ratio was 7.1, which together with the ratio of benzene/NO_x (0.16) gives a ratio of Si/NO_x of 0.067 and a mean exposure of 1.5 $\mu g/m^3$ in ambient air.

Because Si to a large extent exists in large particles, a great part of them will not penetrate into the indoor air. Fifty percent are assumed to penetrate, resulting in a mean population exposure of 0.7 $\mu g/m^3$.

Mean Exposure to Butadiene. Butadiene has not been measured in Sweden, but data in recent years focusing on its genotoxicity call for some attempt to estimate its average concentration. Shan and Singh give mean values of butadiene and benzene that indicate a ratio of 0.2, and thus a mean population exposure of 0.7 $\mu g/m^3$ (20).

Trends

Direct measurements of mutagenic substances in air are seldom made. Therefore, the mean exposure cannot be estimated except by indirect methods. Some indication of the trends in PAH levels, and possibly in ethene and propene levels can be obtained from trends in black-smoke concentration. In the central parts of Gothenburg, the concentrations decreased significantly from 1960 to 1990, probably due to changes in the heating systems, such as introduction of district heating, industrial waste heat recovery, and use of heat pumps (Figure 5). At Fågelroskolan, a school in the northwest part of Gothenburg, and further to the west at the Volvo car production plant in Torslanda, which could be characterized as a peripheral and an industrial suburban area, respectively, the level is lower and the decrease is less. The contribution from the regional background and
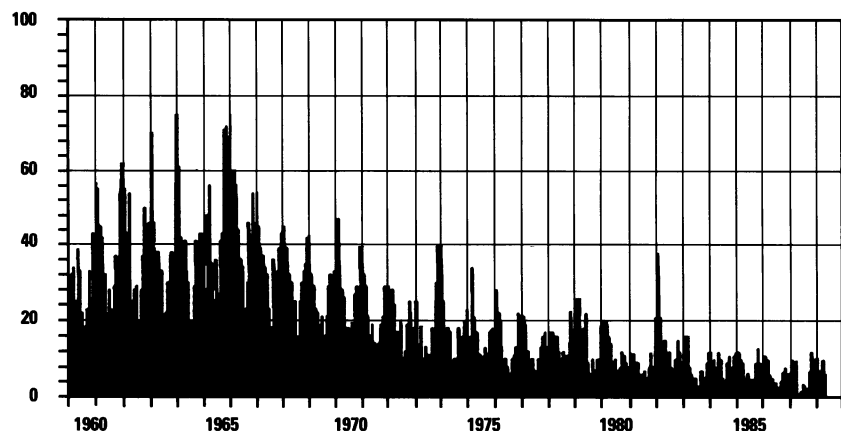

Figure 5. Concentration of black smoke measured in central Gothenburg.

Table 6. Estimate of errors in K-values for PAH in Gothenburg.

K-constant no	SD, %	Number of values	K-error, %
1	50	13	14
2	20	1	20
3	17	3	10
4	40	14	11

traffic may be more important here. The regional black-smoke levels have been measured since 1978 at five stations located in different parts of Sweden in the so-called PMK-net. No changes in black-smoke levels can be detected. Considering that the NO_x levels at Fågelroskolan are of the same magnitude as the average levels in Sweden and considering that the decrease of ground-level emissions from local heating in the Swedish city centers is quite common, it may be reasonable to assume that the mean exposure concentration of mutagenic substances has changed in the same way as the black-smoke concentration at Fågelroskolan. The mean exposure from 1970 would thus be twice as high as the one in 1990. Future exposure levels do not seem to change very much. There is no clear trend in the measured values of black smoke and NO_x in recent years. There are some improvements to be expected in the emission of mutagenic substances from modern cars, but the contributions from malfunctioning cars, regional background levels, and increasing traffic may counteract the effect of these improvements.

Error Analysis

As mentioned earlier, we lack many of the data for estimating exposure to mutagenic substances, and of course, this is also true when trying to estimate the errors in the estimations. Some information is available, however, from the variance in the data used to determine the various ratios that we use in calculation of mean exposures. As mentioned in the section, "Method of Estimating Human Exposure," the mean exposure in a city is determined from the expression:

$$C = K_1 \times K_2 \times K_3 \times K_4 \times CNO_2 \qquad [3]$$

where K_1 is the ratio of the mutagenic substance and NO_x; K_2 is the ratio of winter and year means; K_3 is the ratio of population exposure mean and central city mean; and K_4 is the ratio of NO_x and NO_2.

If we divide the standard deviation in ratio data with the square root of the number of ratio values, we may get an estimation of the error in K-values, as seen in Table 6.

Using the method of least squares, we obtain a total error in terms of twice the standard deviation of 57% for PAH in traffic environments. In our estimation, for PAH in areas with a large emission contribution from small-scale burning of wood and oil, the error will increase. When estimating the exposure in these areas, we were forced to use an indirect method where the error is assumed to be a factor of two, or 100%. The error interval is obtained by dividing and multiplying the given error value with a factor $1 + error \%/100$. (The concentrations in ambient air are usually log normally distributed.)

For ethene we have only two observations of the NO_x ratio, but they differ by only a few percent. However, the contribution from wood burning is made in an indirect way for PAH, and the error is estimated to be the same, i.e., 100%. The error for the estimation of propene is larger, possibly 200%. For benzene, toluene, and xylene, the standard deviation of the K_1 values is on the order of 20%.

Measurements of benzene, toluene, and xylene occur rather frequently in traffic environments, which means that the number of K_1 is large, resulting in a total error estimate of 50% for traffic environments. Because of exposure from other sources in ambient air, such as burning wood and evaporating solvents, the total error is estimated to increase by an extra 20 to 70%. The possible error in estimating the exposure of formaldehyde and acetic aldehyde is estimated to be of the same order of magnitude as that of PAH, i.e., 100%. For Ni, As, Cd, and Si, there are only a few data from which the NO_x ratio can be deduced. Furthermore, we do not know that traffic or common city heating systems are predominant sources of these substances. A total error of 200% may be possible. For asbestos and hexavalent Cr the error may be very large. A guess is a factor of 5 for asbestos and a factor of 10 for hexavalent Cr.

The need for estimation of butadiene exposure was not identified until measurements by the Swedish Urban Project were made. The data used to calculate the NO_x ratio are from a North American database. If we assume that the standard deviation of the NO_x ratio are of the same order of magnitude as for other volatile organic components in this study, an error of 60% is indicated. However the limited quantity of Swedish data call for a somewhat higher error estimate, say 100%.

Discussion

Emissions measurements of light HC, using CO as a tracer, showed that the quantitative

relationship between CO and individual HC was rather stable for unsaturated HC. The relative contributions from diesel-fueled cars (buses and trucks) become more important in the future. The emission of CO from diesel cars is quite low and the emission from passenger cars will be lowered by catalytic cleaning. Thus, the relationship between CO/NO_x and HC will change with time.

It is important to consider the meteorologic parameters when measuring HC, and above all, PAH. The variation for PAH during the year is great—a factor of three to five when comparing winter and summer values.

To make risk assessments, it is necessary to have access to data on the concentration of genotoxic substances. Ambient air monitoring for these substances should be increased in urban areas and in areas with small-scale burning of oil and wood. Since these measurements are very complicated, work should be done to determine which tracer substances or genotoxic substances to monitor in these areas, as well as to harmonize measurement methods and reporting to enable intercomparison of the measurement results.

Through the methods described in this chapter, it is possible only to determine exposure via inhalation. Another important factor for exposure is indirect intake via food. Particulates containing PAH deposit on leafy vegetables and other crops. In this way, cereals can also be an important source for PAH exposure (26). It is an important task to find out in greater detail what the extent of this exposure is, and the main sources of deposited particulates.

Conclusions

The investigations performed show that it is possible to obtain quantitative realtionships between CO and unsaturated HC. Saturated HC and PAH-HC showed greater seasonal variations.

Table 7. Mean exposure to some genotoxic substances in Sweden.

Substance	Mean exposure, yearly mean
Butadiene	$0.7 \ \mu g/m^3$
Ethene	$1.8 \ \mu g/m^3$
Propene	$2.3 \ \mu g/m^3$
Benzene	$3.7 \ \mu g/m^3$
Toluene and xylene	$11 \ \mu g/m^3$
Formaldehyde	$1.2 \ \mu g/m^3$
Acetaldehyde	$1.0 \ \mu g/m^3$
PAH	$19 \ ng/m^3$
Nickel	$2.3 \ ng/m^3$
Chromium (VI)	$0.03 \ ng/m^3$
Arsenic	$7 \ ng/m^3$
Cadmium	$0.2 \ ng/m^3$
Silicon	$0.7 \ ng/m^3$
Asbestos	$200 \ fibers/m^3$ (optical)
	$5,000 \ fibers/m^3$ (electron microscope)

In general, it is important to make more measurements of genotoxic substances in urban areas in a systematic way to get a better basis for risk estimations. Exposure from wood firing and the indirect uptake of PAH via food seem to be important, and more research is needed in those areas.

It is obvious from this investigation that the exposure of mutagenic air pollutants is not a problem only for large cities. Half of the population exposure-dose of NO_x is obtained in cities and urban areas with a population of less than 50,000. If the influence of wood firing and small-scale oil firing is as it appears from the limited data we have, the "median" city is even smaller.

Through use of meteorologic models, data concerning the pattern of human movement and whereabouts, measurement data of NO_2 in urban areas and NO_x as a tracer substance, it has been possible to calculate the mean exposure for a number of genotixic substances. Relationships between NO_x and some genotoxic substances have been determined. The mean exposure of nitrogen oxides for the Swedish population (8.5 million inhabitants) was calculated to be 23 $\mu m/m^3$ as a yearly mean. The results for the mean exposure values to some genotoxic substances in Sweden are summarized in Table 7.

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