2. CHEMISTRY AND ANALYTICAL METHODS

2.1 Physical and chemical properties

Carbon monoxide (CO) is a tasteless, odourless, colourless, non-corrosive and quite stable diatomic molecule that exists as a gas in the Earth’s atmosphere. Radiation in the visible and near-ultraviolet (UV) regions of the electromagnetic spectrum is not absorbed by carbon monoxide, although the molecule does have weak absorption bands between 125 and 155 nm. Carbon monoxide absorbs radiation in the infrared region corresponding to the vibrational excitation of its electronic ground state. It has a low electric dipole moment (0.10 debye), short interatomic distance (0.123 nm) and high heat of formation from atoms or bond strength (2072 kJ/mol). These observations suggest that the molecule is a resonance hybrid of three structures (Perry et al., 1977), all of which contribute nearly equally to the normal ground state. General physical properties of carbon monoxide are given in Table 1.

2.2 Methods for measuring carbon monoxide in ambient air

2.2.1 Introduction

Because of the low levels of carbon monoxide in ambient air, methods for its measurement require skilled personnel and sophisticated analytical equipment. The principles of the methodology have been described by Smith & Nelson (1973). A sample introduction system is used, consisting of a sampling probe, an intake manifold, tubing and air movers. This system is needed to collect the air sample from the atmosphere and to transport it to the analyser without altering the original concentration. It may also be used to introduce known gas concentrations to periodically check the reliability of the analyser output. Construction materials for the sampling probe, intake manifold and tubing should be tested to demonstrate that the test atmosphere composition or concentration is not altered significantly. The sample introduction system should be constructed so that it presents no pressure drop to the analyser. At low flow and low concentrations, such operation may require validation.
### Table 1. Physical properties of carbon monoxide*  

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>28.01</td>
</tr>
<tr>
<td>Critical point</td>
<td>140 °C at 3495.7 kPa</td>
</tr>
<tr>
<td>Melting point</td>
<td>199 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>191.5 °C</td>
</tr>
<tr>
<td>Density at 0 °C, 101.3 kPa</td>
<td>1.250 g/litre</td>
</tr>
<tr>
<td>Density at 25 °C, 101.3 kPa</td>
<td>1.145 g/litre</td>
</tr>
<tr>
<td>Specific gravity relative to air</td>
<td>0.967</td>
</tr>
<tr>
<td>Solubility in water at 0 °C</td>
<td>3.54 ml/100 ml (44.3 ppmm)*</td>
</tr>
<tr>
<td>Solubility in water at 20 °C</td>
<td>2.32 ml/100 ml (29.0 ppmm)*</td>
</tr>
<tr>
<td>Solubility in water at 25 °C</td>
<td>2.14 ml/100 ml (26.8 ppmm)*</td>
</tr>
<tr>
<td>Explosive limits in air</td>
<td>12.5–74.2%</td>
</tr>
<tr>
<td>Fundamental vibration transition</td>
<td>2143.3 cm⁻¹</td>
</tr>
<tr>
<td>Conversion factors at 0 °C, 101.3 kPa</td>
<td>1 mg/m³ = 0.800 ppm*</td>
</tr>
<tr>
<td>Conversion factors at 25 °C, 101.3 kPa</td>
<td>1 ppm = 1.250 mg/m³</td>
</tr>
</tbody>
</table>

* From NRC (1977).

[a] Volume of carbon monoxide is at 0 °C, 1 atm (atmospheric pressure at sea level = 101.3 kPa).

[c] Parts per million by mass (ppmm = g/g).

[d] Parts per million by volume (ppm = mg/litre).

The analyser system consists of the analyser itself and any sample preconditioning components that may be necessary. Sample preconditioning might require a moisture control system to help minimize the false-positive response of the analyser (e.g., the non-dispersive infrared [NDIR] analyser) to water vapour and a particulate filter to help protect the analyser from clogging and possible chemical interference due to particulate buildup in the sample lines or analyser inlet. The sample preconditioning system may also include a flow metering and flow control device to control the sampling rate to the analyser.

A data recording system is needed to record the output of the analyser.
2.2.2 Methods

A reference method or equivalent method for air quality measurements is required for acceptance of measurement data. An equivalent method for monitoring carbon monoxide can be so designated when the method is shown to produce results equivalent to those from the approved reference monitoring method based on absorption of infrared radiation from a non-dispersed beam.

The designated reference methods are automated, continuous methods utilizing the NDIR technique, which is generally accepted as being the most reliable method for the measurement of carbon monoxide in ambient air. As of January 1988, no equivalent methods that use a principle other than NDIR have been designated for measuring carbon monoxide in ambient air.

There have been several excellent reviews on the measurement of carbon monoxide in the atmosphere (National Air Pollution Control Administration, 1970; Driscoll & Berger, 1971; Leithe, 1971; American Industrial Hygiene Association, 1972; NIOSH, 1972; Verdin, 1973; Stevens & Herget, 1974; Harrison, 1975; Schnakenberg, 1976; NRC, 1977; Repp, 1977; Lodge, 1989; OSHA, 1991a; ASTM, 1995; ISO, 1996).

2.2.2.1 Non-dispersive infrared photometry method

Currently, the most commonly used measurement technique is the type of NDIR method referred to as gas filter correlation (Acton et al., 1973; Burch & Gryvnak, 1974; Ward & Zwick, 1975; Burch et al., 1976; Goldstein et al., 1976; Gryvnak & Burch, 1976a,b; Herget et al., 1976; Bartle & Hall, 1977; Chaney & McClenny, 1977).

Carbon monoxide has a characteristic infrared absorption near 4.6 μm. The absorption of infrared radiation by the carbon monoxide molecule can therefore be used to measure the concentration of carbon monoxide in the presence of other gases. The NDIR method is based on this principle (Feldstein, 1967).

Most commercially available NDIR analysers incorporate a gas filter to minimize interferences from other gases. They operate at atmospheric pressure, and the most sensitive analysers are able to detect minimum carbon monoxide concentrations of about 0.05 mg/m³.
(0.044 ppm). Interferences from carbon dioxide and water vapour can be dealt with so as not to affect the data quality. NDIR analysers with detectors as designed by Luft (1962) are relatively insensitive to flow rate, require no wet chemicals, are sensitive over wide concentration ranges and have short response times. NDIR analysers of the newer gas filter correlation type have overcome zero and span problems and minor problems due to vibrations.

2.2.2.2 Gas chromatography method

A more sensitive method for measuring low background levels of carbon monoxide is gas chromatography (Porter & Volman, 1962; Feldstein, 1967; Swinnerton et al., 1968; Bruner et al., 1973; Dagnall et al., 1973; Tesarik & Krejci, 1974; Bergman et al., 1975; Smith et al., 1975; ISO, 1989). This technique is an automated, semi-continuous method in which carbon monoxide is separated from water, carbon dioxide and hydrocarbons other than methane by a stripper column. Carbon monoxide and methane are then separated on an analytical column, and the carbon monoxide is passed through a catalytic reduction tube, where it is converted to methane. The carbon monoxide (converted to methane) passes through a flame ionization detector, and the resulting signal is proportional to the concentration of carbon monoxide in the air. This method has been used throughout the world. It has no known interferences and can be used to measure levels from 0.03 to 50 mg/m$^3$ (0.026 to 43.7 ppm). These analysers are expensive and require continuous attendance by a highly trained operator to produce valid results. For high levels, a useful technique is catalytic oxidation of the carbon monoxide by Hopcalite or other catalysts (Stetter & Blurton, 1976), either with temperature-rise sensors (Naumann, 1975; Schnakenberg, 1976; Benzie et al., 1977) or with electrochemical sensors (Bay et al., 1972, 1974; Bergman et al., 1975; Dempsey et al., 1975; Schnakenberg, 1975; Repp, 1977). Numerous other analytical schemes have been used to measure carbon monoxide in air.

2.2.2.3 Other analysers

Other systems to measure carbon monoxide in ambient air include gas chromatography/flame ionization, in which carbon monoxide is separated from other trace gases by gas chromatography and catalytically converted to methane prior to detection; controlled-potential electrochemical analysis, in which carbon monoxide is
measured by means of the current produced in aqueous solution by its
electro-oxidation by an electro-catalytically active noble metal (the
concentration of carbon monoxide reaching the electrode is controlled
by its rate of diffusion through a membrane, which depends on its
concentration in the sampled atmosphere; Bay et al., 1972, 1974);
galvanic cells that can be used to measure atmospheric carbon
monoxide continuously, in the manner described by Hersch (1964,
1966); coulometric analysis, which employs a modified Hersch-type
cell; mercury replacement, in which mercury vapour formed by the
reduction of mercuric oxide by carbon monoxide is detected
photometrically by its absorption of UV light at 253.7 nm; dual-
isotope fluorescence, which utilizes the slight difference in the
infrared spectra of isotopes of carbon monoxide; catalytic
combustion/thermal detection, which is based on measuring the
temperature rise resulting from catalytic oxidation of the carbon
monoxide in the sample air; second-derivative spectrometry, which
utilizes a second-derivative spectrometer to process the transmission
versus wavelength function of an ordinary spectrometer to produce an
output signal proportional to the second derivative of this function;
and Fourier-transform spectroscopy, which is an extremely powerful
infrared spectroscopic technique.

Intermittent samples may be collected in the field and later
analysed in the laboratory by the continuous analysing techniques
described above. Sample containers may be rigid (glass cylinders or
stainless steel tanks) or non-rigid (plastic bags). Because of location
and cost, intermittent sampling may at times be the only practical
method for air monitoring. Samples can be taken over a few minutes
or accumulated intermittently to obtain, after analysis, either “spot”
or “integrated” results.

Additional techniques for analysing intermittent samples include
colorimetric analysis, in which carbon monoxide reacts in an alkaline
solution with the silver salt of p-sulfamoyl-benzoate to form a
coloured silver sol; a National Institute of Standards and Technology
colorimetric indicating gel (incorporating palladium and molybdenum
salts), which involves colorimetric comparison with freshly prepared
indicating gels exposed to known concentrations of carbon monoxide;
a length-of-stain indicator method, which uses an indicator tube
containing potassium palladosulfite; and frontal analysis, in which air
is passed over an adsorbent until equilibrium is established between
the concentration of carbon monoxide in the air and the concentration of carbon monoxide on the adsorbent.

A simple and inexpensive measurement technique uses detector tubes (indicator tubes) (Leichnitz, 1993). This method is widely applied in industrial hygiene and is suitable for analysis of highly polluted atmospheric air. The measurement with Dräger tubes (Drägerwerk, 1994) is based on the reaction: $5\text{CO} + \text{I}_2 \text{O}_5 \xrightarrow{\text{I}_2} 5\text{CO}_2$. The iodine-coloured layer in the tube corresponds in length to the carbon monoxide concentration in the sample.

### 2.2.3 Measurement using personal monitors

Until the 1960s, most of the data available on ambient carbon monoxide concentrations came from fixed monitoring stations operated routinely in urban areas. The accepted measurement technique was NDIR spectrometry, but the instruments were large and cumbersome, often requiring vibration-free, air-conditioned enclosures. Without a portable, convenient monitor for carbon monoxide, it was extremely difficult to measure carbon monoxide concentrations accurately in the microenvironments that people usually visited.

Ultimately, small personal exposure monitors (PEMs) were developed that could measure carbon monoxide concentrations continuously over time and store the readings automatically on internal digital memories (Ott et al., 1986). These small PEMs made possible the large-scale field studies on human exposure to carbon monoxide in Denver, Colorado, and Washington, DC, USA, in the winter of 1982–83 (Akland et al., 1985).

### 2.2.4 Carbon monoxide detectors/alarms

Carbon monoxide detectors have been designed like residential smoke detectors — to be low cost, yet provide protection from a catastrophic event by sounding an audible alarm. The carbon monoxide detector industry is young, however, and is in a stage of rapid growth. In the USA, an estimated 7–8 million detectors have been purchased since the early 1990s, but the numbers used in homes will continue to rise as local municipalities change building codes to require the installation of carbon monoxide detectors in new residential structures containing combustion-source appliances, stoves or fireplaces.
Currently available carbon monoxide detectors are based on an interactive-type sensor (e.g., tin oxide, Figaro-type gel cell, fuel cell, artificial haemoglobin) that relies on direct interaction between carbon monoxide and the sensitive element in order to generate a response. They are battery-powered, alternating current-powered or both. The most popular alternating current-powered detectors have a heated metallic sensor that reacts with carbon monoxide; the battery-powered detectors have a chemically treated gel disk that darkens with exposure to carbon monoxide or a fuel cell. Small, inexpensive carbon monoxide detection cards or tablets that require frequent visual inspection of colour changes do not sound an alarm and are not recommended as a primary detector.

Carbon monoxide detectors are sensitive to location and environmental conditions, including temperature, relative humidity and the presence of other interfering gases. They may also become less stable with time. For example, they should not be installed in dead-space air (i.e., near ceilings), near windows or near doors where there is a lot of air movement, and they should not be exposed to temperature or humidity extremes. Excessive heat or cold will affect performance, and humidity extremes will affect the activation time. Utilization of non-interactive infrared technology (e.g., NDIR) in indoor carbon monoxide detection would overcome all of the shortcomings of the currently available carbon monoxide detectors.

In the USA, a new voluntary standard for carbon monoxide detectors was published in 1992 by the Underwriters Laboratories (UL Standard 2034) and revised in 1995. This standard provides alarm requirements for detectors that are based on both the carbon monoxide concentration and the exposure time. It is designed so that an alarm is activated within 90 min of exposure to 110 mg/m\(^3\) (100 ppm), within 35 min of exposure to 230 mg/m\(^3\) (200 ppm) or within 15 min of exposure to 460 mg/m\(^3\) (400 ppm) (i.e., when exposures are equivalent to 10% carboxyhaemoglobin [COHb]; see section 2.3). Approximately 15 manufacturers produce detectors listed under UL Standard 2034.

Because UL Standard 2034 covers a wide range of exposure conditions, there has been some ambiguity about its interpretation. For example, it is not clear if a detector meets the standard if the alarm is activated anytime between 5 and 90 min in the presence of 110 mg carbon monoxide/mg\(^3\) (100 ppm). In fact, alarm sensitivities
are still a problem for the industry, and further discussion and direction are needed. Moreover, the 10% carboxyhaemoglobin level is protective of healthy individuals only (see chapter 8). It would be necessary to avoid exposures to 10 mg carbon monoxide/m$^3$ (9 ppm) for 8 h or 29 mg/m$^3$ (25 ppm) for 1 h in order to protect sensitive individuals with coronary heart disease at the 3% carboxyhaemoglobin level. Thus, current detectors provide warning against carbon monoxide levels that are protective of the healthy population only. Despite these limitations, carbon monoxide detectors are reliable and effective, continue to improve and should be recommended for use in homes in addition to smoke detectors and fire alarms.

2.3 Biological monitoring

A unique feature of carbon monoxide exposure is that there is a biological marker of the dose that the individual has received: the level of carbon monoxide in the blood. This level may be calculated by measuring carboxyhaemoglobin in blood or carbon monoxide in exhaled breath.

2.3.1 Blood carboxyhaemoglobin measurement

The level of dissolved carbon monoxide in blood is normally below the level of detection but may be of importance in the transportation of carbon monoxide between cells and tissues (see chapter 6). Thus, the blood level of carbon monoxide is conventionally represented as a percentage of the total haemoglobin available (i.e., the percentage of haemoglobin that is in the form of carboxyhaemoglobin, or simply percent carboxyhaemoglobin).

Any technique for the measurement of carboxyhaemoglobin in blood must be specific and must have sufficient sensitivity and accuracy for the purpose of the values obtained. The majority of technical methods that have been published on measurement of carbon monoxide in blood have been for forensic purposes. These methods are less accurate than generally required for the measurement of low levels of carboxyhaemoglobin (<5%). Blood levels of carbon monoxide resulting from exposure to existing ambient levels of carbon monoxide would not be expected to exceed 5% carboxyhaemoglobin in non-smoking subjects. The focus of the forensic methods has been the reliability of measurements over the
entire range of possible values: from less than 1% to 100% carboxyhaemoglobin. These forensically oriented methods are adequate for the intended use of the values and the non-ideal storage conditions of the samples being analysed.

In the areas of exposure assessment and low-level health effects of carbon monoxide, it is more important to know the accuracy of any method in the low-level range of <5% carboxyhaemoglobin. There is little agreement upon acceptable reference methods in this range, nor are there accurate reference standards available in this range. The use of techniques that have unsubstantiated accuracy in the low range of carboxyhaemoglobin levels can lead to considerable differences in estimations of exposure conditions. Measurement of low levels of carboxyhaemoglobin demands careful evaluation because of the implications, based upon these data, for the setting of air quality standards. Therefore, this section will focus on the methods that have been evaluated at levels below 10% carboxyhaemoglobin and the methods that have been extensively used in assessing exposure to carbon monoxide.

The measurement of carbon monoxide in blood can be accomplished by a variety of techniques, both destructive and non-destructive. Carboxyhaemoglobin can be determined non-destructively by observing the change in the absorption spectrum in either the Soret or visible region brought about by the combination of carbon monoxide with haemoglobin. With present optical sensing techniques, however, all optical methods are limited in sensitivity to approximately 1% of the range of expected values. If attempts are made to expand the lower range of absorbances, sensitivity is lost on the upper end where, in the case of carboxyhaemoglobin, total haemoglobin is measured. For example, in the spectrophotometric method described by Small et al. (1971), a change in absorbance equal to the limit of resolution of 0.01 units can result in a difference in 0.6% carboxyhaemoglobin. Therefore, optical techniques cannot be expected to obtain the resolution that is possible with other means of detection of carbon monoxide (Table 2).

The more sensitive (higher-resolution) techniques require the release of the carbon monoxide from the haemoglobin into a gas phase; the carbon monoxide can then be detected directly by infrared absorption (Maas et al., 1970) following separation using
Table 2. Representative methods for the analysis of carbon monoxide in blood

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
<th>Resolution(^b) (ml/dl)</th>
<th>CV (%)(^c)</th>
<th>Reference method</th>
<th>(r^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasometric detection</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scholander &amp; Roughton</td>
<td>Syringe capillary</td>
<td>0.02</td>
<td>2–4</td>
<td>Van Slyke</td>
<td>ND(^e)</td>
</tr>
<tr>
<td>(1943)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horvath &amp; Roughton</td>
<td>Van Slyke</td>
<td>0.03</td>
<td>6</td>
<td>Van Slyke–Neill</td>
<td>ND</td>
</tr>
<tr>
<td>(1942)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Spectrophotometric detection</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coburn et al. (1964)</td>
<td>Infrared</td>
<td>0.006</td>
<td>1.8</td>
<td>Van Slyke–Syringe</td>
<td>ND</td>
</tr>
<tr>
<td>Small et al. (1971)</td>
<td>Spectrophotometry</td>
<td>0.12</td>
<td>ND</td>
<td>Flame ionization</td>
<td>ND</td>
</tr>
<tr>
<td>Maas et al. (1970)</td>
<td>CO-Oximeter (IL-182)</td>
<td>0.21</td>
<td>5</td>
<td>Spectrophotometric</td>
<td>ND</td>
</tr>
<tr>
<td>Brown (1980)</td>
<td>CO-Oximeter (IL-282)</td>
<td>0.2</td>
<td>5</td>
<td>Flame ionization</td>
<td>0.999</td>
</tr>
<tr>
<td><strong>Gas chromatography</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ayres et al. (1966)</td>
<td>Thermal conductivity</td>
<td>0.001</td>
<td>2</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Goldbaum et al. (1986)</td>
<td>Thermal conductivity</td>
<td>ND</td>
<td>1.35</td>
<td>Flame ionization</td>
<td>0.996</td>
</tr>
<tr>
<td>McCredie &amp; Jose (1967)</td>
<td>Thermal conductivity</td>
<td>0.005</td>
<td>1.8</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dahms &amp; Horvath (1974)</td>
<td>Thermal conductivity</td>
<td>0.006</td>
<td>1.7</td>
<td>Van Slyke</td>
<td>0.983</td>
</tr>
<tr>
<td>Collison et al. (1968)</td>
<td>Flame ionization</td>
<td>0.002</td>
<td>1.8</td>
<td>Van Slyke</td>
<td>ND</td>
</tr>
<tr>
<td>Kane (1985)</td>
<td>Flame ionization</td>
<td>ND</td>
<td>6.2</td>
<td>CO-Oximeter</td>
<td>1.00</td>
</tr>
<tr>
<td>Vreman et al. (1984)</td>
<td>Mercury vapour</td>
<td>0.002</td>
<td>2.2</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

\(^a\) Modified from US EPA (1991d).
\(^b\) The resolution is the smallest detectable amount of carbon monoxide or the smallest detectable difference between samples.
\(^c\) Coefficient of variation (CV) was computed on samples containing less than 15% carboxyhaemoglobin, where possible.
\(^d\) The \(r\) value is the correlation coefficient between the technique reported and the reference method used to verify its accuracy.
\(^e\) ND indicates that no data were available.
gas chromatography, (2) the difference in thermal conductivity between carbon monoxide and the carrier gas (Ayres et al., 1966; McCredie & Jose, 1967; Dahms & Horvath, 1974; Goldbaum et al., 1986; Horvath et al., 1988b; Allred et al., 1989b), (3) the amount of ionization following quantitative conversion of carbon monoxide to methane and ionization of the methane (Collison et al., 1968; Dennis & Valeri, 1980; Guillot et al., 1981; Clerbaux et al., 1984; Kane, 1985; Katsumata et al., 1985; Costantino et al., 1986) or (4) the release of mercury vapour resulting from the combination of carbon monoxide with mercuric oxide (Vreman et al., 1984).

2.3.1.1 Sample handling

Carbon monoxide bound to haemoglobin is a relatively stable compound that can be dissociated by exposure to oxygen or UV radiation (Horvath & Roughton, 1942; Chace et al., 1986). If the blood sample is maintained in the dark under cool, sterile conditions, the carbon monoxide content will remain stable for a long period of time. Various investigators have reported no decrease in percent carboxyhaemoglobin over 10 days (Collison et al., 1968), 3 weeks (Dahms & Horvath, 1974), 4 months (Ocak et al., 1985) and 6 months (Vreman et al., 1984). The blood collection system used can influence the carbon monoxide level, because some ethylenediamine-tetraacetic acid vacutainer tube stoppers contain carbon monoxide (Vreman et al., 1984). The stability of the carbon monoxide content in properly stored samples does not indicate that constant values will be obtained by all techniques of analysis. The spectrophotometric methods are particularly susceptible to changes in optical qualities of the sample, resulting in small changes in carboxyhaemoglobin with storage (Allred et al., 1989b).

Therefore, the care needed to make a carboxyhaemoglobin determination depends upon the technique that is being utilized. It appears as though measurement of low levels of carboxyhaemoglobin with optical techniques should be conducted as soon as possible following collection of the samples.

2.3.1.2 Potential reference methods

Exposure to carbon monoxide at equilibrium conditions results in carboxyhaemoglobin levels of between 0.1 and 0.2% for each milligram of carbon monoxide per cubic metre air (part per million).
A reference technique for the measurement of carboxyhaemoglobin should be able to discriminate between two blood samples with a difference of 0.1% carboxyhaemoglobin (approximately 0.02 ml/dl). To accomplish this task, the coefficient of variation (standard deviation of repeated measures on any given sample divided by the mean of the values times 100) of the method should be less than 5%, so that the two values that are different by 0.1 percentage points can be statistically proven to be distinct. In practical terms, a reference method should have the sensitivity to detect approximately 0.025% carboxyhaemoglobin to provide this level of confidence in the values obtained.

The accurate measurement of carboxyhaemoglobin requires the quantitation of the content of carbon monoxide released from haemoglobin in the blood. Optically based techniques have limitations of resolution and specificity due to the potential interference from many sources. The techniques that can be used as reference methods involve the quantitative release of carbon monoxide from the haemoglobin followed by the measurement of the amount of carbon monoxide released. Classically, this quantitation was measured manometrically with a Van Slyke apparatus (Horvath & Roughton, 1942) or a Roughton-Scholander syringe (Roughton & Root, 1945). These techniques have served as the “Gold Standard” in this field for almost 50 years. However, there are limitations of resolution with these techniques at the lower ranges of carboxyhaemoglobin. The gasometric standard methodology has been replaced with headspace extraction followed by the use of solid-phase gas chromatographic separation with several different types of detection: thermal conductivity, flame ionization and mercury vapour reduction. The carbon monoxide in the headspace can also be quantitated by infrared detection, which can be calibrated with gas standards. However, there is no general agreement that any of the more sensitive methods of carbon monoxide analysis are acceptable reference methods.

The following techniques all conform to all the requirements of a reference method:

1. **Flame ionization detection:** This technique requires the separation of carbon monoxide from the other headspace gases and the reduction of the carbon monoxide to methane by catalytic reduction.
(2) **Thermal conductivity detection:** This technique uses vacuum extraction of carbon monoxide from blood in a Van Slyke apparatus and gas chromatographic separation with thermal conductivity analysis of the carbon monoxide.

(3) **Infrared detection:** This technique uses a method for extracting carbon monoxide from blood under normal atmospheric conditions and then injecting the headspace gas into an infrared analyser.

The conventional means of representing the quantity of carbon monoxide in a blood sample is the percent carboxyhaemoglobin: the percentage of the total carbon monoxide combining capacity that is in the form of carboxyhaemoglobin. This is conventionally determined by the use of the following formula:

\[
\% \text{COHb} = \left[ \frac{\text{CO content}}{(Hb \times 1.389)} \right] \times 100
\]

where \( \text{CO content} \) is the carbon monoxide concentration, measured in millilitres per decilitre blood at standard temperature and pressure, dry; \( Hb \) is the haemoglobin concentration, measured in grams per decilitre blood; and 1.389 is the stoichiometric combining capacity of carbon monoxide for haemoglobin in units of millilitres of carbon monoxide per gram of haemoglobin at standard temperature and pressure, dry; however, in practice, a value of 1.36 ml carbon monoxide/g haemoglobin is used for the oxygen capacity of normal human blood because it is impossible to achieve 100% haemoglobin saturation.

The analytical methods that quantify the carbon monoxide content in blood require the conversion of these quantities to percent carboxyhaemoglobin. The product of the haemoglobin and the theoretical combining capacity (1.389, according to International Committee for Standardization in Haematology, 1978) yields the carbon monoxide capacity. With the use of capacity and the measured content, the percentage of carbon monoxide capacity (percent carboxyhaemoglobin) is calculated. To be absolutely certain of the accuracy of the haemoglobin measurement, the theoretical value should be routinely substantiated by direct measurement (internal validation) of the haemoglobin–carbon monoxide combining capacity. The total carbon monoxide–haemoglobin combining capacity should be determined as accurately as the content of carbon monoxide. The error of the techniques that measure carbon monoxide content is
dependent on the error in haemoglobin analysis for the final form of the data, percent carboxyhaemoglobin. Therefore, the actual carbon monoxide–haemoglobin combining capacity should be measured and compared with the calculated value based upon the reference method for haemoglobin measurement. The measurement of carbon monoxide–haemoglobin combining capacity can be routinely performed by equilibration of a blood sample with carbon monoxide (Allred et al., 1989b).

The standard methods for haemoglobin determination involve the conversion of all species of haemoglobin to cyanomethaemoglobin with the use of a mixture of potassium ferricyanide, potassium cyanide and sodium bicarbonate.

2.3.1.3 Other methods of measurement

There is a wide variety of other techniques that have been described for the analysis of carbon monoxide in blood. These methods include UV-visible spectrophotometry (Small et al., 1971; Brown, 1980; Zwart et al., 1984, 1986), magnetic circular dichroism spectropolarimetry (Wigfield et al., 1981), photochemistry (Sawicki & Gibson, 1979), gasometric methods (Horvath & Roughton, 1942; Roughton & Root, 1945) and a calorimetric method (Sjostrand, 1948a). Not all of these methods have been as well characterized for the measurement of low levels of carboxyhaemoglobin as those listed above as potential reference methods.

1) Spectrophotometric methods

The majority of the techniques are based upon optical detection of carboxyhaemoglobin, which is more rapid than the reference techniques because it does not involve extraction of the carbon monoxide from the blood sample. These direct measurements also enable the simultaneous measurement of several species of haemoglobin, including reduced haemoglobin, oxyhaemoglobin (O₂Hb) and carboxyhaemoglobin. The limitations of the spectrophotometric techniques have been reviewed by Kane (1985). The optical methods utilizing UV wavelengths require dilution of the blood sample, which can lead to the loss of carbon monoxide as a result of competition with the dissolved oxygen in solution. Removing the dissolved oxygen with dithionite can lead to the formation of sulphaemoglobin, which interferes with the measurement of carboxyhaemoglobin (Rai & Minty,
Another limitation is that the absorption maxima (and spectral curves) are not precisely consistent between individuals. This may be due to slight variations in types of haemoglobin in subjects. For these reasons, the techniques using fixed-wavelength measurement points would not be expected to be as precise, accurate or specific as the proposed reference methods mentioned above.

2) CO-Oximeter measurements of carboxyhaemoglobin

The speed of measurement and relative accuracy of spectrophotometric measurements over the entire range of expected values led to the development of CO-Oximeters. These instruments utilize from two to seven wavelengths in the visible region for the determination of proportions of oxyhaemoglobin, carboxyhaemoglobin, reduced haemoglobin and methaemoglobin. The proportion of each species of haemoglobin is determined from the absorbance and molar extinction coefficients at present wavelengths. All of the commercially available instruments provide rapid results for all the species of haemoglobin being measured. In general, the manufacturers’ listed limit of accuracy for all of the instruments is 1% carboxyhaemoglobin. However, this level of accuracy is not suitable for measurements associated with background carbon monoxide levels (<2% carboxyhaemoglobin) because it corresponds to errors exceeding 50%. The precision of measurement for these instruments is excellent and has misled users regarding the accuracy of the instruments. The relatively modest level of accuracy is adequate for the design purposes of the instruments; however, at low levels of carboxyhaemoglobin, the ability of the instruments to measure the percent carboxyhaemoglobin accurately is limited.

2.3.2 Carbon monoxide in expired breath

Carbon monoxide levels in expired breath can be used to estimate the levels of carbon monoxide in the subject’s blood. The basic determinants of carbon monoxide levels in alveolar air have been described by Douglas et al. (1912), indicating that there are predictable equilibrium conditions that exist between carbon monoxide bound to haemoglobin and the partial pressure of the carbon monoxide in the blood. The equilibrium relationship for carbon monoxide between blood and the gas phase to which the blood is exposed can be described as follows:
\[ \frac{P_{\text{CO}}}{P_{\text{O}_2}} = M \left( \% \text{COHb} / \% \text{O}_2\text{Hb} \right) \] (2-2)

where \( P_{\text{CO}} \) is the partial pressure of carbon monoxide in the blood, \( P_{\text{O}_2} \) is the partial pressure of oxygen in the blood, \( M \) is the Haldane coefficient (reflecting the relative affinity of haemoglobin for oxygen and carbon monoxide), \( \% \text{COHb} \) is the percentage of total haemoglobin combining capacity bound with carbon monoxide, and \( \% \text{O}_2\text{Hb} \) is the percentage of total haemoglobin combining capacity bound with oxygen.

The partial pressure of carbon monoxide in the arterial blood will reach a steady-state value relative to the partial pressure of carbon monoxide in the alveolar gas. Therefore, by measuring the end-expired breath from a subject’s lungs, one can measure the end-expired carbon monoxide partial pressure and, with the use of the Haldane relationship, estimate the blood level of carboxyhaemoglobin. This measurement will always be an estimate, because the Haldane relationship is based upon attainment of an equilibrium, which does not occur under physiological conditions.

The measurement of carbon monoxide levels in expired breath to estimate blood levels is based upon application of the Haldane relationship to gas transfer in the lung (Eq. 2-2). For example, when the oxygen partial pressure is increased in the alveolar gas, it is possible to predict the extent to which the partial pressure of carbon monoxide will increase in the alveolar gas. This approach is limited, however, because of the uncertainty associated with variables that are known to influence gas transfer in the lung and that mediate the direct relationship between liquid-phase gas partial pressures and air-phase partial pressures.

The basic mechanisms that are known to influence carbon monoxide transfer in the lung have been identified through the establishment of techniques to measure pulmonary diffusion capacity for carbon monoxide. Some of the factors that can result in decreased diffusion capacity for carbon monoxide (altering the relationship between expired carbon monoxide pressures and carboxyhaemoglobin levels) are increased membrane resistance, intravascular resistance, age, alveolar volume, pulmonary vascular blood volume, pulmonary blood flow and ventilation/perfusion inequality (Forster, 1964). The extent to which each of these variables actually contributes to the
variability in the relationship has not been experimentally demonstrated. There are few experiments that focus on the factors leading to variability in the relationship between alveolar carbon monoxide and percent carboxyhaemoglobin at the levels of carboxyhaemoglobin currently deemed to be of regulatory importance. This may be due in part to the difficulties in working with analytical techniques, particularly blood techniques, that are very close to their limits of reproducibility.

The expired breath method for obtaining estimates of blood levels of carbon monoxide has a distinct advantage for monitoring large numbers of subjects, because of the non-invasive nature of the method. Other advantages include the ability to obtain an instantaneous reading and the ability to take an immediate replicate sample for internal standardization. The breath-holding technique for enhancing the normal carbon monoxide concentration in exhaled breath has been widely used; however, it should be noted that the absolute relationship between breath-hold carbon monoxide pressures and blood carbon monoxide pressures has not been thoroughly established for carboxyhaemoglobin levels below 5%. The breath-holding method allows time (20 s) for diffusion of carbon monoxide into the alveolar air so that carbon monoxide levels are higher than levels following normal tidal breathing.

Partial pressures of carbon monoxide in expired breath are highly correlated with percent carboxyhaemoglobin levels over a wide range of carboxyhaemoglobin levels. The accuracy of the breath-hold method is unknown owing to the lack of paired sample analyses of carbon monoxide partial pressures in exhaled breath and concurrent carboxyhaemoglobin levels in blood utilizing a sensitive reference method. No one has attempted to determine the error of estimate involved in applying group average regression relationships to the accurate determination of carboxyhaemoglobin. Therefore, the extrapolation of breath-hold carbon monoxide partial pressures to actual carboxyhaemoglobin levels must be made with reservation until the accuracy of this method is better understood.

2.3.2.1 Measurement methods

Ventilation in healthy individuals involves air movement through areas in the pulmonary system that are primarily involved in either conduction of gas or gas exchange in the alveoli. In a normal breath (tidal volume), the proportion of the volume in the non-gas exchang-
ing area is termed the dead space. In the measurement of carbon monoxide in the exhaled air, the dead-space gas volume serves to dilute the alveolar carbon monoxide concentration. Several methods have been developed to account for the dead-space dilution. These include the mixed expired gas technique, which uses the Bohr equation to determine the physiological dead space; the breath-hold technique, a method of inspiration to total lung capacity followed by a breath-hold period of various durations (a breath-hold time of 20 s was found to provide near-maximal values for carbon monoxide pressures); and the rebreathing technique, in which 5 litres of oxygen are rebreathed for 2–3 min while the carbon dioxide is removed.

Kirkham et al. (1988) compared all three techniques for measuring expired carbon monoxide to predict percent carboxyhaemoglobin. The rebreathing and breath-hold methods both yield approximately 20% higher levels of “alveolar” carbon monoxide than does the Bohr computation from mixed expired gas. Both the mixed expired and breath-holding techniques show a significant decline in the alveolar carbon monoxide tension when the subject is standing. Therefore, measurements of expired carbon monoxide must be made in the same body position relative to control measurements or reference measurements.

2.3.2.2 Potential limitations

The measurement of exhaled breath has the advantages of ease, speed, precision and greater subject acceptance over measurement of blood carboxyhaemoglobin. However, the accuracy of the breath measurement procedure and the validity of the Haldane relationship between breath and blood at low environmental carbon monoxide concentrations remain in question.
3. SOURCES OF CARBON MONOXIDE IN THE ENVIRONMENT

3.1 Introduction

Carbon monoxide is produced by both natural and anthropogenic processes. About half of the carbon monoxide is released at the Earth’s surface, and the rest is produced in the atmosphere. Many papers on the global sources of carbon monoxide have been published over the last 20 years; whether most of the carbon monoxide in the atmosphere is from human activities or from natural processes has been debated for nearly as long.

The recent budgets that take into account previously published data suggest that human activities are responsible for about 60% of the carbon monoxide in the non-urban troposphere, and natural processes account for the remaining 40%. It also appears that combustion processes directly produce about 40% of the annual emissions of carbon monoxide (Jaffe, 1968, 1973; Robinson & Robbins, 1969, 1970; Swinnerton et al., 1971), and oxidation of hydrocarbons makes up most of the remainder (about 50%) (Went, 1960, 1966; Rasmussen & Went, 1965; Zimmerman et al., 1978; Hanst et al., 1980; Greenberg et al., 1985), along with other sources such as the oceans (Swinnerton et al., 1969; Seiler & Junge, 1970; Lamontagne et al., 1971; Linnenbom et al., 1973; Liss & Slater, 1974; Seiler, 1974; Seiler & Schmidt, 1974; Swinnerton & Lamontagne, 1974; NRC, 1977; Bauer et al., 1980; Logan et al., 1981; DeMore et al., 1985) and vegetation (Krall & Tolbert, 1957; Wilks, 1959; Siegel et al., 1962; Seiler & Junge, 1970; Bidwell & Fraser, 1972; Seiler, 1974; NRC, 1977; Seiler & Giehl, 1977; Seiler et al., 1978; Bauer et al., 1980; Logan et al., 1981; DeMore et al., 1985). Some of the hydrocarbons that eventually end up as carbon monoxide are also produced by combustion processes, constituting an indirect source of carbon monoxide from combustion. These conclusions are summarized in Table 3, which is adapted from the 1981 budget of Logan et al., in which most of the previous work was incorporated (Logan et al., 1981; WMO, 1986). The total emissions of carbon monoxide are about 2600 million tonnes per year. Other budgets by Volz et al. (1981) and by Seiler & Conrad (1987) have been reviewed by Warneck (1988). Global emissions between 2000 and 3000 million tonnes per year are consistent with these budgets.
Sources of Carbon Monoxide in the Environment

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<th>Anthropogenic</th>
<th>Natural</th>
<th>Global</th>
<th>Range</th>
</tr>
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<td></td>
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<tr>
<td>Fossil fuels</td>
<td>500</td>
<td>—</td>
<td>500 400–1000</td>
</tr>
<tr>
<td>Forest clearing</td>
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<td>—</td>
<td>400 200–800</td>
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<td>Savanna burning</td>
<td>200</td>
<td>—</td>
<td>200 100–400</td>
</tr>
<tr>
<td>Wood burning</td>
<td>50</td>
<td>—</td>
<td>50 25–150</td>
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<td>—</td>
<td>30</td>
<td>30 10–50</td>
</tr>
<tr>
<td>Oxidation of hydrocarbons</td>
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</tr>
<tr>
<td>Methane</td>
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<td>300</td>
<td>600 400–1000</td>
</tr>
<tr>
<td>Non-methane hydrocarbons</td>
<td>90</td>
<td>600</td>
<td>690 300–1400</td>
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<td>Other sources</td>
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<tr>
<td>Plants</td>
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<td>100</td>
<td>100 50–200</td>
</tr>
<tr>
<td>Oceans</td>
<td>—</td>
<td>40</td>
<td>40 20–80</td>
</tr>
<tr>
<td>Totals (rounded)</td>
<td>1500</td>
<td>1100</td>
<td>2600 2000–3000</td>
</tr>
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</table>

* Adapted from Logan et al. (1981) and revisions reported by the WMO (1986).
* All estimates are expressed to one significant figure. The sums are rounded to two significant digits.
* Half the production of carbon monoxide from the oxidation of methane is attributed to anthropogenic sources and the other half to natural sources based on the budget of methane from Khalil & Rasmussen (1984c).

3.2 Principles of formation by source category

Carbon monoxide is produced in the atmosphere by reactions of hydroxyl radicals with methane and other hydrocarbons, both anthropogenic and natural, as well as by the reactions of alkenes with ozone and of isoprene and terpenes with hydroxyl radicals and ozone.

Carbon monoxide is also produced at the Earth’s surface during the combustion of fuels. The burning of any carbonaceous fuel produces two primary products: carbon dioxide and carbon monoxide. The production of carbon dioxide predominates when the air or oxygen supply is in excess of the stoichiometric needs for complete combustion. If burning occurs under fuel-rich conditions, with less air or oxygen than is needed, carbon monoxide will be produced in abundance. In past years, most of the carbon monoxide and carbon
dioxide formed were simply emitted into the atmosphere. In recent years, concerted efforts have been made to reduce ambient air concentrations of materials that are potentially harmful to humans. Much carbon monoxide, most notably from mobile sources, is converted to carbon dioxide, which is then emitted into the atmosphere.

Emission source categories in the USA (US EPA, 1991b) are divided into five individual categories: (1) transportation, (2) stationary source fuel combustion, (3) industrial processes, (4) solid waste disposal and (5) miscellaneous.

Transportation sources include emissions from all mobile sources, including highway and off-highway motor vehicles. Highway motor vehicles include passenger cars, trucks, buses and motorcycles. Off-highway vehicles include aircraft, locomotives, vessels and miscellaneous engines such as farm equipment, industrial and construction machinery, lawnmowers and snowmobiles.

Emission estimates from gasoline- and diesel-powered motor vehicles are based upon vehicle-mile (vehicle-kilometre) tabulations and emission factors. Eight vehicle categories are considered: (1) light-duty gasoline vehicles (mostly passenger cars), (2) light-duty diesel passenger cars, (3) light-duty gasoline trucks (weighing less than 6000 lb [2.7 tonnes]), (4) light-duty gasoline trucks (weighing 6000–8500 lb [2.7–3.9 tonnes]), (5) light-duty diesel trucks, (6) heavy-duty gasoline trucks and buses, (7) heavy-duty diesel trucks and buses and (8) motorcycles. The emission factors used are based on the US Environmental Protection Agency’s (EPA) mobile source emission factor model, developed by the EPA Office of Mobile Sources, which uses the latest available data to estimate average in-use emissions from highway vehicles.

Aircraft emissions are based on emission factors and aircraft activity statistics reported by the Federal Aviation Administration (1988). Emissions are based on the number of landing–take-off cycles. Any emissions in cruise mode, which is defined to be above 3000 ft (1000 m), are ignored. Average emission factors for each year, which take into account the national mix of aircraft types for general aviation, military and commercial aircraft, are used to compute the emissions.
In the USA, the Department of Energy reports consumption of diesel fuel and residual fuel oil by locomotives (US Department of Energy, 1988a). Average emission factors applicable to diesel fuel consumption were used to calculate emissions. Vessel use of diesel fuel, residual oil and coal is also reported by the Department of Energy (US Department of Energy, 1988a,b). Gasoline use is based on national boat and motor registrations, coupled with a use factor (gallons [litres] per motor per year) (Hare & Springer, 1973) and marine gasoline sales (US Department of Transportation, 1988). Emission factors from EPA Report No. AP-42 are used to compute emissions (US EPA, 1985).

Gasoline and diesel fuel are consumed by off-highway vehicles in substantial quantities. The fuel consumption is divided into several categories (e.g., farm tractors, other farm machinery, construction equipment, industrial machinery, snowmobiles and small general utility engines such as lawnmowers and snowblowers). Fuel use is estimated for each category from estimated equipment population and an annual use factor of gallons (litres) per unit per year (Hare & Springer, 1973), together with reported off-highway diesel fuel deliveries (US Department of Energy, 1988a) and off-highway gasoline sales (US Department of Transportation, 1988).

Stationary combustion equipment, such as coal-, gas- or oil-fired heating or power generating plants, generates carbon monoxide as a result of improper or inefficient operating practices or inefficient combustion techniques. The specific emission factors for stationary fuel combustors vary according to the type and size of the installation and the fuel used, as well as the mode of operation. The US EPA’s compilation of air pollutant emission factors provides emission data obtained from source tests, material balance studies, engineering estimates and so forth for the various common emission categories. For example, coal-fired electricity generating plants report coal use to the US Department of Energy (1988b,c). Distillate oil, residual oil, kerosene and natural gas consumed by stationary combustors are also reported by user category to the US Department of Energy (1988a). Average emission factors from EPA Report No. AP-42 (US EPA, 1985) were used to calculate the emission estimates. The consumption of wood in residential wood stoves has likewise been estimated by the US Department of Energy (1982, 1984).
In addition to fuel combustion, certain other industrial processes generate and emit varying quantities of carbon monoxide into the air. The lack of published national data on production, type of equipment and controls, as well as an absence of emission factors, makes it impossible to include estimates of emissions from all industrial process sources.

Solid waste carbon monoxide emissions result from the combustion of wastes in municipal and other incinerators, as well as from the open burning of domestic and municipal refuse.

Miscellaneous carbon monoxide emissions result from the burning of forest and agricultural materials, smouldering coal refuse materials and structural fires.

The Forest Service of the US Department of Agriculture publishes information on the number of forest fires and the acreage burned (US Forest Service, 1988). Estimates of the amount of material burned per acre are made to determine the total amount of material burned. Similar estimates are made to account for managed burning of forest areas. Average emission factors were applied to the quantities of materials burned to calculate emissions.

A study was conducted by the US EPA (Yamate, 1974) to obtain, from local agricultural and pollution control agencies, estimates of the number of acres and estimated quantity of material burned per acre in agricultural burning operations. These data have been updated and used to estimate agricultural burning emissions, based on average emission factors.

Estimates of the number of burning coal refuse piles existing in the USA are made in reports by the Bureau of Mines. McNay (1971) presents a detailed discussion of the nature, origin and extent of this source of pollution. Rough estimates of the quantity of emissions were obtained using this information by applying average emission factors for coal combustion. It was assumed that the number of burning refuse piles decreased to a negligible level by 1975.

The US Department of Commerce publishes, in its statistical abstracts, information on the number and types of structures damaged by fire (US Department of Commerce, 1987). Emissions were
Sources of Carbon Monoxide in the Environment

estimated by applying average emission factors for wood combustion to these totals.

The estimated total annual carbon monoxide emissions from the various source categories in the USA for 1970, 1975 and 1980–1990 (US EPA, 1991b) indicate that carbon monoxide emissions from all anthropogenic sources declined from 101.4 million tonnes (111.8 million short tons) in 1970 to 60.1 million tonnes (66.2 million short tons) in 1990. The majority, about 63%, of the carbon monoxide emissions total comes from transportation sources, 12% comes from stationary source fuel combustion, 8% comes from industrial processes, 3% comes from solid waste and 14% comes from miscellaneous sources.

The single largest contributing source of carbon monoxide emissions is highway vehicles, which emitted an estimated 50% of the national total in 1990. Because of the implementation of the Federal Motor Vehicle Control Program, carbon monoxide emissions from highway vehicles declined 54%, from 65.3 to 30.3 million tonnes, in the period 1970–1990. Fig. 1 displays the trend in estimated carbon monoxide emissions from the major highway vehicle categories from 1970 to 1990. Although the total annual vehicle-miles (vehicle-kilometres) travelled continue to increase in the USA (by 37% just in the period 1981–1990), total carbon monoxide emissions from highway vehicles have continued to decrease as a result of the Federal Motor Vehicle Control Program-mandated air pollution control devices on new vehicles.

Carbon monoxide emissions from other sources have also generally decreased. In 1970, emissions from burning of agricultural crop residues were greater than in more recent years. Solid waste disposal emissions have also decreased as the result of implementation of regulations limiting or prohibiting burning of solid waste in many areas. Emissions of carbon monoxide from stationary source fuel combustion occur mainly from the residential sector. These emissions were reduced somewhat through the mid-1970s as residential consumers converted to natural gas, oil or electric heating equipment. Recent growth in the use of residential wood stoves has reversed this trend, but increased carbon monoxide emissions from residential sources continue to be small compared with highway vehicle emissions. Nevertheless, in 1990, residential wood combustion accounted for
Fig. 1. Estimated emission of carbon monoxide from gasoline-fuelled highway vehicles in the USA (adapted from US EPA, 1991a).
Sources of Carbon Monoxide in the Environment

about 10% of national carbon monoxide emissions, more than any source category except highway vehicles. Carbon monoxide emissions from industrial processes have generally been declining since 1970 as the result of the obsolescence of a few high-polluting processes such as manufacture of carbon black by the channel process and installation of controls on other processes.

Considerable effort has been made to reduce emissions of carbon monoxide and other pollutants to the atmosphere. Because the automobile engine is recognized to be the major source of carbon monoxide in most urban areas, special attention is given to the control of automotive emissions. Generally, the approach has been technological: reduction of carbon monoxide emissions to the atmosphere either by improving the efficiency of the combustion processes, thereby increasing the yield of carbon dioxide and decreasing the yield of carbon monoxide, or by applying secondary catalytic combustion reactors to the waste gas stream to convert carbon monoxide to carbon dioxide.

The development and application of control technology to reduce emissions of carbon monoxide from combustion processes generally have been successful and are continuing to receive deserved attention. The reduction of carbon monoxide emissions from 7.0 to 3.4 g/mi (from 4.4 to 2.1 g/km), scheduled for the 1981 model year, was delayed 2 years, reflecting in part the apparent difficulty encountered by the automobile industry in developing and supplying the required control technology. The carbon monoxide emission limit for light-duty vehicles at low altitude has been 3.4 g/mi (2.1 g/km) since 1983; since 1984, this limit has applied to light-duty vehicles at all altitudes.

Carbon monoxide emissions from 1990 to 1994 in Germany, as estimated by the Federal Environmental Agency (1997), are summarized in Table 4 and show a clear reduction with time. The estimated carbon monoxide emissions in Europe during 1990 are summarized in Table 5, including the sum of 28 European countries and individual data from 10 countries (European Environmental Agency, 1995). The Task Group noted that the original reference does not specify any details concerning the zero values listed in Table 5.
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<td>kt</td>
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<tr>
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<td>10 743</td>
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<td>9 046</td>
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<td>7 926</td>
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<th>Germany</th>
<th>Italy</th>
<th>Netherlands</th>
<th>Poland</th>
<th>Romania</th>
<th>Spain</th>
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<td>Commercial, institutional and residential combustion</td>
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<tr>
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<td>582</td>
<td>6 812</td>
<td>5 892</td>
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Table 5. Carbon monoxide emission estimates in Europe in 1990
Table 5 (contd).

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<th>Italy</th>
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<td></td>
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<tr>
<td>Other mobile sources</td>
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<td>Waste treatment and</td>
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<td>3 187</td>
<td>4 977</td>
<td>1 349</td>
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</table>

* From European Environmental Agency (1995).

b NE = no estimate.
3.2.1 General combustion processes

Incomplete combustion of carbon-containing compounds creates varying amounts of carbon monoxide. The chemical and physical processes that occur during combustion are complex because they depend not only on the type of carbon compound reacting with oxygen, but also on the conditions existing in the combustion chamber (Pauling, 1960; Mellor, 1972). Despite the complexity of the combustion process, certain general principles regarding the formation of carbon monoxide from the combustion of hydrocarbon fuels are accepted widely.

Gaseous or liquid hydrocarbon fuel reacts with oxygen in a chain of reactions that result in the formation of carbon monoxide. Carbon monoxide then reacts with hydroxyl radicals to form carbon dioxide. The second reaction is approximately 10 times slower than the first. In coal combustion, too, the reaction of carbon and oxygen to form carbon monoxide is one of the primary reactions, and a large fraction of carbon atoms go through the carbon monoxide form. Again, the conversion of carbon monoxide to carbon dioxide is much slower.

Four basic variables control the concentration of carbon monoxide produced in the combustion of all hydrocarbon fuels: (1) oxygen concentration, (2) flame temperature, (3) gas residence time at high temperatures and (4) combustion chamber turbulence. Oxygen concentration affects the formation of both carbon monoxide and carbon dioxide, because oxygen is required in the initial reactions with the fuel molecule and in the formation of the hydroxyl radical. As the availability of oxygen increases, more complete conversion of carbon monoxide to carbon dioxide results. Flame and gas temperatures affect both the formation of carbon monoxide and the conversion of carbon monoxide to carbon dioxide, because both reaction rates increase exponentially with increasing temperature. Also, the hydroxyl radical concentration in the combustion chamber is very temperature dependent. The conversion of carbon monoxide to carbon dioxide is also enhanced by longer residence time, because this is a relatively slow reaction in comparison with carbon monoxide formation. Increased gas turbulence in the combustion zones increases the actual reaction rates by increasing the mixing of the reactants and assisting the relatively slower gaseous diffusion process, thereby resulting in more complete combustion.
3.2.2 Combustion engines

3.2.2.1 Mobile combustion engines

Most mobile sources of carbon monoxide are internal combustion engines of two types: (1) gasoline-fuelled, spark ignition, reciprocating engines (carburetted or fuel-injected) and (2) diesel-fuelled reciprocating engines. The carbon monoxide emitted from any given engine is the product of the following factors: (1) the concentration of carbon monoxide in the exhaust gases, (2) the flow rate of exhaust gases and (3) the duration of operation.

1) Internal combustion engines (gasoline-fuelled, spark ignition engines)

Exhaust concentrations of carbon dioxide increase with lower (richer) air-to-fuel (A/F) ratios and decrease with higher (leaner) A/F ratios, but they remain relatively constant with ratios above the stoichiometric ratio of about 15:1 (Hagen & Holiday, 1964). The behaviour of gasoline automobile engines before and after the installation of pollutant control devices differs considerably. Depending on the mode of driving, the average uncontrolled engine operates at A/F ratios ranging from about 11:1 to a point slightly above the stoichiometric ratio. During the idling mode, at low speeds with light load (such as low-speed cruise), during the full open throttle mode until speed picks up and during deceleration, the A/F ratio is low in uncontrolled cars, and carbon monoxide emissions are high. At higher-speed cruise and during moderate acceleration, the reverse is true. Cars with exhaust controls generally remain much closer to stoichiometric A/F ratios in all modes, and thus the carbon monoxide emissions are kept lower. The exhaust flow rate increases with increasing engine power output.

The decrease in available oxygen with increasing altitude has the effect of enriching the A/F mixture and increasing carbon monoxide emissions from carburetted engines. Fuel-injected gasoline engines, which predominate in the vehicle fleet today, have more closely controlled A/F ratios and are designed and certified to comply with applicable emission standards regardless of elevation (US EPA, 1983).

Correlations between total emissions of carbon monoxide in grams per vehicle-mile (vehicle-kilometre) and average route speed show a decrease in emissions with increasing average speed.
Sources of Carbon Monoxide in the Environment

(Simonaitis & Heicklen, 1972; Stuhl & Niki, 1972; US EPA, 1985). During low-speed conditions (below 32 km/h or 20 mi/h average route speed), the greater emissions per unit of distance travelled are attributable to (1) an increased frequency of acceleration, deceleration and idling encountered in heavy traffic and (2) the consequent increase in the operating time per mile (kilometre) driven.

The carbon monoxide and the unburned hydrocarbon exhaust emissions from an uncontrolled engine result from incomplete combustion of the fuel–air mixture. Emission control on new vehicles is being achieved by engine modifications, improvements in engine design and changes in engine operating conditions. Substantial reductions in carbon monoxide and other pollutant emissions result from consideration of design and operating factors such as leaner, uniform mixing of fuel and air during carburetion, controlled heating of intake air, increased idle speed, retarded spark timing, improved cylinder head design, exhaust thermal reactors, oxidizing and reducing catalysts, secondary air systems, exhaust recycle systems, electronic fuel injection, A/F ratio feedback controls and modified ignition systems (NAS, 1973).

2) Internal combustion engines (diesel engines)

Diesel engines are in use throughout the world in heavy-duty vehicles, such as trucks and buses, and they are also extensively used in Western Europe in light-duty vans, taxis and some cars. Diesel engines allow more complete combustion and use less volatile fuels than do spark ignition engines. The operating principles are significantly different from those of the gasoline engine. In diesel combustion, carbon monoxide concentrations in the exhaust are relatively low because high temperature and large excesses of oxygen are involved in normal operation.

3.2.2.2 Stationary combustion sources (steam boilers)

This section refers to fuel-burning installations such as coal-, gas- or oil-fired heating or power generating plants (external combustion boilers).

In these combustion systems, the formation of carbon monoxide is lowest at a ratio near or slightly above the stoichiometric A/F ratio. At lower than stoichiometric A/F ratios, high carbon monoxide
concentrations reflect the relatively low oxygen concentration and the possibility of poor reactant mixing from low turbulence. These two factors can increase emissions even though flame temperatures and residence time are high. At higher than stoichiometric A/F ratios, increased carbon monoxide emissions result from decreased flame temperatures and shorter residence time. These two factors remain predominant even when oxygen concentrations and turbulence increase. Minimal carbon monoxide emissions and maximum thermal efficiency therefore require combustor designs that provide high turbulence, sufficient residence time, high temperatures and near-stoichiometric A/F ratios. Combustor design dictates the actual approach to that minimum.

### 3.2.3 Other sources

There are numerous industrial activities that result in the emission of carbon monoxide at one or more stages of the process (Walsh & Nussbaum, 1978; US EPA, 1979a, 1985). Manufacturing pig iron can produce as much as 700–1050 kg carbon monoxide/tonne of pig iron. Other methods of producing iron and steel can produce carbon monoxide at a rate of 9–118.5 kg/tonne. However, most of the carbon monoxide generated is normally recovered and used as fuel. Conditions such as “slips,” abrupt collapses of cavities in the coke–ore mixture, can cause instantaneous emissions of carbon monoxide that temporarily exceed the capacity of the control equipment. Grey iron foundries can produce 72.5 kg carbon monoxide/tonne of product, but an efficient afterburner can reduce the carbon monoxide emissions to 4.5 kg/tonne. Nevertheless, industrial carbon monoxide emissions may constitute an important part of total emissions in industrial cities — for example, in the Ruhr area in Germany.

Charcoal production results in average carbon monoxide emissions of 172 kg/tonne. Emissions from batch kilns are difficult to control, although some may have afterburners. Afterburners can more easily reduce, by an estimated 80% or more, the relatively constant carbon monoxide emissions from continuous charcoal production. Emissions from carbon black manufacture can range from 5 to 3200 kg carbon monoxide/tonne depending on the efficiency and quality of the emission control systems.

Some chemical processes, such as phthalic anhydride production, give off as little as 6 kg carbon monoxide/tonne with proper controls.
Sulfate pulping for paper produces 1–30 kg carbon monoxide/tonne, lime manufacturing normally produces 1–4 kg carbon monoxide/tonne, and carbon monoxide emissions from adipic acid production are zero or slight with proper controls. Other industrial chemical processes that cause carbon monoxide emissions are the manufacture of terephthalic acid and the synthesis of methanol and higher alcohols. As a rule, most industries find it economically desirable to install suitable controls to reduce carbon monoxide emissions.

Even though some of these carbon monoxide emission rates seem excessively high, they are, in fact, only a small part of the total pollutant load. Mention of these industries is made to emphasize the concern for localized pollution problems when accidents occur or proper controls are not used.

In some neighbourhoods, wintertime carbon monoxide emissions include a significant component from residential fireplaces and wood stoves. Emissions of carbon monoxide can range from 18 to 140 g/kg, depending on design, fuel type and skill of operation.

Although the estimated carbon monoxide emissions resulting from forest wildfires in the USA have fluctuated between about 4 and 9 million tonnes per year since 1970 and were 6.2 million tonnes in 1989, the estimated total carbon monoxide emissions from industrial processes in the USA declined from 8.9 million tonnes in 1970 to 4.6 million tonnes in 1989 (US EPA, 1991c).

3.3 Indoor carbon monoxide

3.3.1 Introduction

Carbon monoxide is introduced to indoor environments through emissions from a variety of combustion sources and in the infiltration or ventilation air from outdoors. The resulting indoor concentration, both average and peak, is dependent on a complex interaction of several interrelated factors affecting the introduction, dispersion and removal of carbon monoxide. These factors include, for example, such variables as (1) the type, nature (factors affecting the generation rate
of carbon monoxide) and number of sources, (2) source use characteristics, (3) building characteristics, (4) infiltration or ventilation rates, (5) air mixing between and within compartments in an indoor space, (6) removal rates and potential remission or generation by indoor surfaces and chemical transformations, (7) existence and effectiveness of air contaminant removal systems and (8) outdoor concentrations.

Source emissions from indoor combustion are usually characterized in terms of emission rates, defined as the mass of pollutant emitted per unit of fuel input (micrograms per kilojoule). They provide source strength data as input for indoor modelling, promote an understanding of the fundamental processes influencing emissions, guide field study designs assessing indoor concentrations, identify and rank important sources and aid in developing effective mitigation measures. Unfortunately, source emissions can vary widely. Although it would be most useful to assess the impact of each of the sources on indoor air concentrations of carbon monoxide by using models, the high variability in the source emissions and in other factors affecting the indoor levels does not make such an effort very useful. Such an estimate will result in predicted indoor concentrations ranging over several orders of magnitude, making them of no practical use, and may be misleading.

3.3.2 Emissions from indoor sources

Carbon monoxide emitted directly into the indoor environment is one of several air contaminants resulting from combustion sources. Such emissions into occupied spaces can be unintentional or the result of accepted use of unvented or partially vented combustion sources. Faulty or leaky flue pipes, backdrafting and spillage from combustion appliances that draw their air from indoors (e.g., Moffatt, 1986), improper use of combustion sources (e.g., use of a poorly maintained kerosene heater) and air intake into a building from attached parking garages are all examples of unintentional or accidental indoor sources of carbon monoxide. In the USA, the National Center for Health Statistics (1986) estimates that between 700 and 1000 deaths per year are due to accidental carbon monoxide poisoning. Mortality statistics are similar for other developed countries as well. The number of individuals experiencing severe adverse health effects at sublethal carbon monoxide concentrations from accidental indoor sources is no doubt many times the number of estimated deaths. Although the
unintentional or accidental indoor sources of carbon monoxide represent a serious health hazard, little is known about the extent of the problem throughout the world. Such sources cannot be characterized for carbon monoxide emissions in any standard way that would make the results extendable to the general population.

The major indoor sources of carbon monoxide emissions that result from the accepted use of unvented or partially vented combustion sources include gas cooking ranges and ovens, gas appliances, unvented gas space heaters, unvented kerosene space heaters, coal- or wood-burning stoves and cigarette combustion.

3.3.2.1 Gas cooking ranges, gas ovens and gas appliances

Estimates indicate that gas (natural gas and liquid propane) is used for cooking, heating water and drying clothes in approximately 45.1% of all homes in the USA (US Bureau of the Census, 1982) and in nearly 100% of the homes in some other countries (e.g., the Netherlands). Unvented, partially vented and improperly vented gas appliances, particularly the gas cooking range and oven, represent an important source category of carbon monoxide emissions into the indoor residential environment. Emissions of carbon monoxide from these gas appliances are a function of a number of variables relating to the source type (range top or oven, water heater, dryer, number of pilot lights, burner design, etc.), source condition (age, maintenance, combustion efficiency, etc.), source use (number of burners used, frequency of use, fuel consumption rate, length of use, improper use, etc.) and venting of emissions (existence and use of outside vents over ranges, efficiency of vents, venting of gas dryers, etc.).

The source emission studies typically have been conducted in the laboratory setting and have involved relatively few gas ranges and gas appliances. The reported studies indicate that carbon monoxide emissions are highly variable among burners on a single gas cooking range and between gas cooking ranges and ovens, varying by as much as an order of magnitude. Operating a gas cooking range or oven under improperly adjusted flame conditions (yellow-tipped flame) can result in greater than a fivefold increase in emissions compared with properly operating flame conditions (blue flame). Use of a rich or lean fuel appeared to have little effect on carbon monoxide emissions. In general, carbon monoxide emissions were roughly, on average, comparable for top burners, ovens, pilot lights and unvented gas
dryers when corrected for fuel consumption rate. The emission rates
gathered by either the direct or mass balance method were
comparable. Only one study attempted to evaluate gas stove emissions
in the field for a small number (10) of residences. This study found
carbon monoxide emissions to be as much as a factor of 4 higher than
in chamber studies. Given the prevalence of the source, limited field
measurements and poor agreement between existing laboratory- and
field-derived carbon monoxide emission data, there is a need to
establish a better carbon monoxide emission database for gas cooking
ranges in residential settings.

3.3.2.2 Unvented space heaters

Unvented kerosene and gas space heaters are used in the colder climates to supplement central heating systems or in more moderate climates as the primary source of heat. During the heating season, space heaters generally will be used for a number of hours during the day, resulting in emissions over relatively long periods of time.

Over the last several years, there has been a dramatic increase in the use of unvented or poorly vented kerosene space heaters in residential and commercial establishments, primarily as a supplemental heat source. For example, in the USA, an estimated 16.1 million such heaters had been sold through 1986 (S.E. Womble, personal communication, US Consumer Product Safety Commission, 1988). An additional 3 million residences use unvented gas space heaters (fuelled by natural gas or propane). The potentially large number of unvented space heaters used throughout the world, particularly during periods when energy costs rise quickly, makes them an important source of carbon monoxide indoors.

Carbon monoxide emissions from unvented kerosene and gas space heaters can vary considerably and are a function of heater design (convective, radiant, combination, etc.), condition of heater and manner of operation (e.g., flame setting).

Carbon monoxide emissions from unvented gas space heaters were found to be variable from heater to heater, but were roughly comparable to those for gas cooking ranges. Infrared gas space heaters produced higher emissions than the convective or catalytic heaters. Emissions of carbon monoxide for these heaters were higher for maladjusted heaters and for the mass balance versus direct method of
testing. No differences for rich or lean fuel were found, but use of natural gas resulted in higher emissions than did use of propane. Lower fuel consumption settings resulted in lower carbon monoxide emissions. Emissions were observed to vary in time during a heater run and increase when room or chamber oxygen levels decreased.

Among the three principal unvented kerosene space heater designs (radiant, convective and two-stage burners), radiant heaters produced the highest carbon monoxide emissions and convective heaters produced the lowest emissions. Wick setting (low, normal or high) had a major impact on emissions, with the low-wick setting resulting in the highest carbon monoxide emissions. Data from different laboratories are in good agreement for this source.

3.3.2.3 Coal or wood stoves

Use of coal- or wood-burning stoves has been a popular cost savings alternative to conventional cooking and heating systems using gas or oil. Carbon monoxide and other combustion by-products enter the indoor environment during fire start-up, during fire-tending functions or through leaks in the stove or venting system. Hence, it is difficult to evaluate indoor carbon monoxide emission rates for these sources. Traynor et al. (1987) evaluated indoor carbon monoxide levels from four wood-burning stoves (three airtight stoves and one non-airtight stove) in a residence. The non-airtight stove emitted substantial amounts of carbon monoxide to the residence, particularly when operated with a large fire. The airtight stoves contributed considerably less. The average carbon monoxide source strengths during stove operation ranged from 10 to 140 cm$^3$/h for the airtight stoves and from 220 to 1800 cm$^3$/h for the non-airtight stoves.

3.3.2.4 Tobacco combustion

The combustion of tobacco represents an important source of indoor air contaminants. Carbon monoxide is emitted indoors from tobacco combustion through the exhaled mainstream smoke and from the smouldering end of the cigarette (sidestream smoke). Carbon monoxide emission rates in mainstream and sidestream smoke have been evaluated extensively in small chambers (less than a litre in volume) using a standardized smoking machine protocol. The results of these studies have been summarized and evaluated in several reports (e.g., NRC, 1986a; Surgeon General of the United States,
1986). These results indicate considerable variability in total (mainstream plus sidestream smoke) carbon monoxide emissions, with a typical range of 40–67 mg per cigarette. A small chamber study of 15 brands of Canadian cigarettes (Rickert et al., 1984) found the average carbon monoxide emission rate (mainstream plus sidestream smoke) to be 65 mg per cigarette. A more limited number of studies have been done using large chambers with the occupants smoking or using smoking machines. Girman et al. (1982) reported a carbon monoxide emission rate of 94.6 mg per cigarette for a large chamber study in which one cigarette brand was evaluated. A carbon monoxide emission factor of 88.3 mg per cigarette was reported by Moschandreas et al. (1985) for a large chamber study of one reference cigarette.

On average, a smoker smokes approximately two cigarettes per hour, with an average smoking time of approximately 10 min per cigarette. Using the above range of reported carbon monoxide emission rates for environmental tobacco smoke, this would roughly result in the emission of 80–190 mg of carbon monoxide per smoker per hour into indoor spaces where smoking occurs. This value compares with an approximate average carbon monoxide emission rate of 260–545 mg/h for one range-top burner (without pilot light) operating with a blue flame. Two smokers in a house would produce hourly carbon monoxide emissions comparable to the hourly production rate of a single gas burner. Tobacco combustion therefore represents an important indoor source of carbon monoxide, particularly in locations where many people are smoking.
4. ENVIRONMENTAL DISTRIBUTION AND TRANSFORMATION

4.1 Introduction

Carbon monoxide was first discovered to be a minor constituent of the Earth’s atmosphere in 1948 by Migeotte (1949). While taking measurements of the solar spectrum, he observed a strong absorption band in the infrared region at 4.6 μm, which he attributed to carbon monoxide (Lagemann et al., 1947). On the twin bases of the belief that the solar contribution to that band was negligible and his observation of a strong day-to-day variability in absorption, Migeotte (1949) concluded that an appreciable amount of carbon monoxide was present in the terrestrial atmosphere of Columbus, Ohio, USA. In the 1950s, many more observations of carbon monoxide were made, with measured concentrations ranging from 0.09 to 110 mg/m³ (0.08 to 100 ppm) (Migeotte & Neven, 1952; Benesch et al., 1953; Locke & Herzberg, 1953; Faith et al., 1959; Robbins et al., 1968; Sie et al., 1976). On the basis of these and other measurements available in 1963, Junge (1963) stated that carbon monoxide appeared to be the most abundant trace gas, other than carbon dioxide, in the atmosphere. The studies of Sie et al. (1976) indicated higher mixing ratios near the ground than in the upper atmosphere, implying a source in the biosphere, but Junge (1963) emphasized that knowledge of the sources and sinks of atmospheric carbon monoxide was extremely poor. It was not until the late 1960s that concerted efforts were made to determine the various production and destruction mechanisms for carbon monoxide in the atmosphere.

Far from human habitation in remote areas of the southern hemisphere, natural background carbon monoxide concentrations average around 0.05 mg/m³ (0.04 ppm), primarily as a result of natural processes such as forest fires and the oxidation of methane. In the northern hemisphere, background concentrations are 2–3 times higher because of more extensive human activities. Much higher concentrations occur in cities, arising from technological sources such as automobiles and the production of heat and power. Carbon monoxide emissions are increased when fuel is burned in an incomplete or inefficient way.
The physical and chemical properties of carbon monoxide suggest that its atmospheric removal occurs primarily by reaction with hydroxyl radicals. Almost all the carbon monoxide emitted into the atmosphere each year is removed by reactions with hydroxyl radicals (85%), by soils (10%) and by diffusion into the stratosphere. There is a small imbalance between annual emissions and removal, causing an increase of about 1% per year. It is very likely that the imbalance is due to increasing emissions from anthropogenic activities. The average concentration of carbon monoxide is about 100 : g/m$^3$ (90 ppbv), which amounts to about 400 million tonnes in the atmosphere, and the average lifetime is about 2 months. This view of the global cycle of carbon monoxide is consistent with the present estimates of average hydroxyl radical concentrations and the budgets of other trace gases, including methane and methyl chloroform.

4.2 Global sources, sinks and lifetime

The largest sources of carbon monoxide in the global atmosphere are combustion processes and the oxidation of hydrocarbons (see chapter 3). The mass balance of a trace gas in the atmosphere can be described as a balance between the rate of change of the global burden added to the annual rate of loss on the one side and global emissions on the other side ($dC/dt + \text{loss rate} = \text{source emissions}$, where $C$ = concentration). In steady state, the atmospheric lifetime ($\tau$) is the ratio of the global burden to the loss rate. The global burden is the total number of molecules of a trace gas in the atmosphere or its total mass. The concentration of a trace gas can vary ($dC/dt$ is not 0) when either the loss rate or the emissions vary cyclically in time, representing seasonal variations, or vary over a long time, often representing trends in human industrial activities or population. For carbon monoxide, both types of trends exist. There are large seasonal cycles driven mostly by seasonal variations in the loss rate but also affected by seasonal variations in emissions, and there are also indications of long-term trends probably caused by increasing anthropogenic emissions.

4.2.1 Sinks

It is believed that reaction with hydroxyl radicals is the major sink for removing carbon monoxide from the atmosphere. The cycle of the hydroxyl radical itself cannot be uncoupled from the cycles of carbon monoxide, methane, water and ozone. In the troposphere,
Environmental Distribution and Transformation

Hydroxyl radicals (OH\(_A\)) are produced by the photolysis of ozone (h\(\nu\) + O\(_3\) \rightarrow O\((^1D) + O\)) followed by the reaction of the excited oxygen atoms with water vapour to produce two hydroxyl radicals (O\((^1D) + H_2O \rightarrow 2OH\)). The production of hydroxyl radicals is balanced by their removal principally by reactions with carbon monoxide and methane. On a global scale, carbon monoxide may remove more hydroxyl radicals than methane; however, methane is more important in the southern hemisphere, where there is much less carbon monoxide, than in the northern hemisphere, but the amount of methane is only slightly less in the northern hemisphere.

The amount of carbon monoxide that is removed by reactions with hydroxyl radicals can be estimated by calculating the loss as

\[ \text{loss} = K_{eff} [OH\_A\_ave] [CO\_ave], \]

where \(K_{eff}\) is the effective reaction rate constant, \([OH\_A\_ave]\) is the average hydroxyl radical concentration and \([CO\_ave]\) is the average concentration of carbon monoxide. The reaction rate constant of CO + OH\(_A\) is \(K = (1.5 \times 10^{-13}) (1 + 0.6 P_{atm}) \text{ cm}^3/\text{molecule per second}\) (DeMore et al., 1987), where \(P_{atm}\) is the atmospheric pressure. The constant \(K_{eff}\) describes the effective reaction rate, taking into account the decreasing atmospheric pressure and decreasing carbon monoxide concentrations with height. Estimating \(K_{eff}\) to be \(2 \times 10^{-13} \text{ cm}^3/\text{molecule per second}\) and taking \([OH\_A\_ave]\) to be \(8 \times 10^5 \text{ molecules/cm}^3\) and \([CO\_ave]\) to be 90 ppbv (equivalent to about 100 \(\mu\)g/m\(^3\)), the annual loss of carbon monoxide from reactions with hydroxyl radicals is about 2200 million tonnes per year. The values adopted for \([OH\_A\_ave]\) and \([CO\_ave]\) are discussed in more detail later in this chapter.

Uptake of carbon monoxide by soils has been documented and may amount to about 250 million tonnes per year, or about 10% of the total emitted into the atmosphere (Inman et al., 1971; Ingersoll et al., 1974; Seiler & Schmidt, 1974; Bartholomew & Alexander, 1981), although arid soils may release carbon monoxide into the atmosphere (Conrad & Seiler, 1982). Another 100 million tonnes (5%) or so are probably removed annually in the stratosphere (Seiler, 1974).

4.2.2 Atmospheric lifetime

Based on the global sources and sinks described above, the average atmospheric lifetime of carbon monoxide can be calculated to be about 2 months, with a range between 1 and 4 months, which reflects the uncertainty in the annual emissions of carbon monoxide.
(J = C/S, where C is the tropospheric mixing ratio and S is the total annual emissions). The lifetime, however, can vary enormously with latitude and season compared with its global average value. During winters at high and middle latitudes, carbon monoxide has a lifetime of more than a year, but during summers at middle latitudes, the lifetime may be closer to the average global lifetime of about 2 months. Moreover, in the tropics, the average lifetime of carbon monoxide is probably about 1 month. These calculated variations reflect the seasonal cycles of hydroxyl radicals at various latitudes.

4.2.3 Latitudinal distribution of sources

When the sources, sinks, transport and observed concentrations of carbon monoxide are combined into a mass balance model, it is possible to calculate any one of these four components if the others are known. In the case of carbon monoxide, the sources can be estimated assuming that the sinks (hydroxyl radical reaction and soils), transport and concentrations are known. The latitudinal distribution of sources can be described in a one-dimensional model (Khalil & Rasmussen, 1990b). This model is similar to that described by Czeplak & Junge (1974) and Fink & Klais (1978). A time-averaged version was applied to the carbon monoxide budget by Hameed & Stewart (1979), and a somewhat modified and time-dependent version, mentioned above, was applied by Khalil & Rasmussen (1990b) to derive the latitudinal distribution of carbon monoxide shown in Fig. 2. Calculations by Khalil & Rasmussen (1990b) also suggest that emissions are higher in spring and summer than in the other seasons, particularly in the middle northern latitudes. This is expected for three reasons: (1) oxidation of methane and other hydrocarbons is faster during the summer because of the seasonal variation of hydroxyl radicals; (2) other direct emissions are also greater during spring and summer; and (3) at middle and higher latitudes, methane and non-methane hydrocarbons build up during the winter, and this reservoir is oxidized when hydroxyl radical concentrations rise during the spring.

From Fig. 2, the emissions from the northern and southern tropical latitudes sum up to 480 million tonnes per year and 330 million tonnes per year, respectively; the emissions from the northern and southern middle latitudes are 960 million tonnes per year and 210 million tonnes per year, respectively; some 50 million tonnes are emitted each year from the Arctic; and some 10 million tonnes per year come from the Antarctic. The largest fluxes of carbon monoxide
4.2.4 Uncertainties and consistencies

The first consistency one notes is that the total emissions of carbon monoxide estimated from the various sources are balanced by the estimated removal of carbon monoxide. The approximate balance between sources and sinks is expected because the trends are showing an increase of only about 4–8 million tonnes per year compared with...
the total global emission rate of more than 2000 million tonnes per year.

On the other hand, there are large uncertainties in the sources and sinks that in the future may upset the apparently cohesive present budget of carbon monoxide. Although the patterns of the global distribution are becoming established, there are still uncertainties about the absolute concentrations. Estimates of emissions from individual sources are very uncertain (see Table 3 in chapter 3). In most cases, the stated uncertainty is a qualitative expression of the likely range of emissions, and it cannot be interpreted statistically. Therefore, the resulting uncertainty in the total emissions, obtained by adding up the uncertainties in individual sources, appears to be large.

There are two difficulties encountered in improving the estimates of carbon monoxide emissions from individual sources. First, although many critical experiments to determine the production and emissions of carbon monoxide from individual sources are yet to be done, there is a limit to the accuracy with which laboratory data can be extrapolated to the global scale. Second, the cycle of carbon monoxide may be so intimately tied up with the cycles of hydrocarbons that accurate global estimates of carbon monoxide emissions may not be possible until the hydrocarbon cycles are better understood.

Whereas the global distribution and seasonal variations in the global distribution of hydroxyl radicals can be calculated, there are no direct measurements of hydroxyl radicals that can be used to estimate the removal of carbon monoxide. The effective average concentration of hydroxyl radicals that acts on trace gases can be estimated indirectly from the cycles of other trace gases with known global emissions. Therefore, the total emissions of carbon monoxide are constrained by the budgets of other trace gases, even though the estimates of emissions from individual sources may remain uncertain. The most notable constraint may be the budget of methyl chloroform. Methyl chloroform is a degreasing solvent that has been emitted into the atmosphere in substantial quantities for more than 20 years. It is thought to be removed principally by reacting with hydroxyl radicals and to a lesser extent by photodissociation in the stratosphere. Because industry records on methyl chloroform production and sales have been kept for a long time, methyl chloroform can be used to estimate the average amount of hydroxyl radicals needed to explain the observed concentrations compared with the emissions. The
accuracy of the source estimates of methyl chloroform is improved by
the patterns of its uses; most methyl chloroform tends to be released
shortly after purchase, so large unknown or unquantified reservoirs
probably do not exist. The recent budgets of methyl chloroform
suggest that, on average, there are about $8 \times 10^5$ molecules of
hydroxyl radical per cubic centimetre, although significant
uncertainties remain (see, for example, Khalil & Rasmussen, 1984c).
This is the value used above in estimating the loss of carbon
monoxide from reaction with hydroxyl radicals. The same average
value of hydroxyl radicals also explains the methane concentrations
compared with estimated sources, lending more support to the
accuracy of the estimated hydroxyl radical concentrations. Neither of
these constraints is very stringent; however, if the total global
emissions of carbon monoxide from all sources are much different
from the estimated 2600 million tonnes per year, then revisions of the
budgets of both methane and methyl chloroform may be required.

Although there are other sources and sinks of carbon monoxide,
these are believed to be of lesser importance on a global scale (Swin-
nerton et al., 1971; Chan et al., 1977).

4.3 Global distributions

Atmospheric concentrations, and thus the global distribution, are
generally the most accurately known components of a global mass
balance of a trace gas, because direct atmospheric measurements can
be taken (Wilkniss et al., 1973; Seiler, 1974; Ehhalt & Schmidt,
1978; Pratt & Falconer, 1979; Heidt et al., 1980; Dianov-Klokov &
Yurganov, 1981; Seiler & Fishman, 1981; Rasmussen & Khalil,
1982; Reichle et al., 1982; Hoell et al., 1984; Fraser et al., 1986;
Khalil & Rasmussen, 1988, 1990). Much has been learned about the
global distribution of carbon monoxide over the last decade. The
experiments leading to the present understanding range from
systematic global observations at ground level for the last 8–10 years,
reported by Khalil & Rasmussen (1988, 1990a) and Seiler (Seiler &
Junge, 1970; Seiler, 1974), to finding the instantaneous global
distribution of carbon monoxide from remote-sensing instruments on
board the US National Aeronautics and Space Administration’s space
shuttle, as reported by Reichle et al. (1982, 1990).
4.3.1 Seasonal variations

The seasonal variations in carbon monoxide are well established (Dianov-Klokov & Yurganov, 1981; Seiler et al., 1984; Fraser et al., 1986; Khalil & Rasmussen, 1990a). High concentrations are observed during the winters in each hemisphere, and the lowest concentrations are seen in late summer. The amplitude of the cycle is largest at high northern latitudes and diminishes as one moves towards the equator until it is reversed in the southern hemisphere, reflecting the reversal of the seasons. The seasonal variations are small in the equatorial region. These patterns are expected from the seasonal variations in hydroxyl radical concentrations and carbon monoxide emissions. At mid and high latitudes, diminished solar radiation, water vapour and ozone during winters cause the concentrations of hydroxyl radicals to be much lower than during summer. The removal of carbon monoxide is slowed down, and its concentrations build up. In summer, the opposite pattern exists, causing the large seasonal variations in carbon monoxide.

On the hemispheric scale, the seasonal variation in carbon monoxide is approximately proportional to the concentration. Therefore, because there is much more carbon monoxide in the northern hemisphere than in the southern hemisphere, the decline of concentrations in the northern hemisphere during the summer is not balanced by the rise of concentrations in the southern hemisphere. This causes a global seasonal variation. The total amount of carbon monoxide in the Earth’s atmosphere undergoes a remarkably large seasonal variation; the global burden is highest during northern winters and lowest during northern summers.

4.3.2 Latitudinal variation

The global seasonal variation in carbon monoxide content in the Earth’s atmosphere also creates a seasonal variation in the latitudinal distribution (Newell et al., 1974; Seiler, 1974; Reichle et al., 1982, 1986; Khalil & Rasmussen, 1988, 1990a). During northern winters, carbon monoxide levels are at their highest in the northern hemisphere, whereas concentrations in the southern hemisphere are at a minimum. The interhemispheric gradient, defined as the ratio of the amounts of carbon monoxide in the northern and southern hemispheres, is at its maximum of about 3.2 during northern hemisphere winters and falls to about 1.8 during northern hemisphere summers.
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which is about half the winter value. The average latitudinal gradient is about 2.5, which means that, on average, there is about 2.5 times as much carbon monoxide in the northern hemisphere as in the southern hemisphere. Early data on latitudinal variations did not account for the seasonal variations.

4.3.3 Variations with altitude

In the northern hemisphere troposphere, the concentrations of carbon monoxide generally decline with altitude, but in the southern hemisphere, the vertical gradient may be reversed as a result of the transport of carbon monoxide from the northern hemisphere into the southern hemisphere. Above the tropopause, concentrations decline rapidly, so that there is very little carbon monoxide between 20 and 40 km; at still higher altitudes, the mixing ratio may again increase (Seiler & Junge, 1969; Seiler & Warneck, 1972; Fabian et al., 1981).

4.3.4 Other variations

The concentration of carbon monoxide is generally higher in the air over populated continental areas than in the air over oceans, even though oceans release carbon monoxide into the atmosphere. Other regions, such as tropical forests, may also be a source of isoprene and other hydrocarbons that may form carbon monoxide in the atmosphere. Such sources produce shifting patterns of high carbon monoxide concentrations over regional and perhaps even larger spatial scales. Variations in carbon monoxide concentrations were measured during the 1984 flights of the space shuttle, as reported by Reichle et al. (1990).

Occasionally, significant diurnal variations in carbon monoxide concentrations may also occur in some locations. For instance, diurnal variations have been observed over some parts of the oceans, with high concentrations during the day and low concentrations at night. Because similar patterns also exist in the surface seawater, the diurnal variations in carbon monoxide concentrations in the air can be explained by emissions from the oceans.

Finally, after the repeating cycles and other trends are subtracted, considerable random fluctuations still remain in time series of measurements. These fluctuations reflect the short lifetime of carbon
monoxide and the vicinity of the sources, and they complicate the
detection of long-term trends.

4.4 Global trends

Global concentrations of carbon monoxide were reported to be
increasing during the late 1970s and early 1980s, because some 60% of the
global emissions of carbon monoxide come from anthropogenic
sources, which had increasing emissions over this period. Direct
atmospheric observations reported by Khalil & Rasmussen (1984a)
showed a detectable increasing trend at Cape Meares in Oregon, USA,
between 1979 and 1982, when the rate of increase was about 5% per
year. Subsequent data from the same site showed that the rate was not
sustained for long, and a much smaller increasing trend of somewhat
less than 2% per year emerged over the longer period of 1970–1987
(Khalil & Rasmussen, 1988). Similar data from other sites distributed
worldwide also showed a global increase of about 1% per year (Khalil
& Rasmussen, 1988). The trends were strongest in the mid-northern
latitudes where most of the sources were located and became smaller
and weaker in the southern hemisphere. At the mid-southern latitude
site, the trends persisted but were not statistically significant (Khalil
& Rasmussen, 1988). Rinsland & Levine (1985) reported estimates of
carbon monoxide concentrations from spectroscopic plates from
Europe showing that between 1950 and 1984, carbon monoxide
concentrations increased at about 2% per year. Spectroscopic
measurements of carbon monoxide taken by Dvoryashina et al. (1982,
1984) and Dianov-Klokov and colleagues (Dianov-Klokov et al.,
1978; Dianov-Klokov & Yurganov, 1981) in the Soviet Union also
suggested an increase of about 2% per year between 1974 and 1982
(Khalil & Rasmussen, 1984b, 1988).

More recent reports of carbon monoxide measurements in air
samples show that from 1988 to 1993, global carbon monoxide
concentrations started to decline rapidly. Novelli et al. (1994) col-
lected air samples from 27 locations between 71 °N and 41 °S about
once every 3 weeks from a ship during the period June 1990 to June
1993. In the northern latitudes, carbon monoxide concentrations
decreased at a spatially and temporally average rate of 8.4 ± 1.0:
g/m³ (7.3 ± 0.9 ppb) per year (6.1% per year). In the southern
latitudes, carbon monoxide concentrations decreased at a rate of 4.8
± 0.6 : g/m³ (4.2 ± 0.5 ppb) per year (7.0% per year). Khalil &
Rasmussen (1994) reported a slightly smaller decline in global carbon
monoxide concentrations of 2.6 ± 0.8% per year during the period from 1988 to 1992. The rate of decrease reported by Khalil & Rasmussen (1994) was particularly rapid in the southern hemisphere. The authors hypothesize that this decline may reflect a reduction in tropical biomass burning.

Since 1993, the downward trend in global carbon monoxide concentrations has levelled off, and it is not clear if carbon monoxide will continue to decline or increase. These reported trends in global carbon monoxide concentrations are relatively small, and the random variability is large. Nevertheless, they are extremely important towards an understanding of global atmospheric chemistry and possible effects on global climate. Such changes in tropospheric carbon monoxide concentrations can cause shifts in hydroxyl radical concentrations and affect the oxidizing capacity of the atmosphere, thereby influencing the concentration of other trace gases, including methane. This change could also be a significant factor contributing to levels of ozone in the non-urban troposphere.

The likely future global-scale concentrations of carbon monoxide are completely unknown at present. It is possible that in the next decade, carbon monoxide concentrations will remain stable or even decline further. Emissions from automobiles are probably on the decline worldwide, emissions from biomass burning may be stabilizing or even declining, as speculated above, and the contribution from methane oxidation may no longer be increasing as rapidly as before. Because the atmospheric lifetime of carbon monoxide is short compared with those of other contributors to global change, the ambient concentrations adjust rapidly to existing emissions of carbon monoxide or its precursors.
5. ENVIRONMENTAL LEVELS AND PERSONAL EXPOSURES

5.1 Introduction

Air quality guidelines for carbon monoxide are designed to protect against actual and potential human exposures in ambient air that would cause adverse health effects. The World Health Organization’s guidelines for carbon monoxide exposure (WHO, 1987) are expressed at four averaging times, as follows:

- 100 mg/m$^3$ for 15 min
- 60 mg/m$^3$ for 30 min
- 30 mg/m$^3$ for 1 h
- 10 mg/m$^3$ for 8 h

The guideline values and periods of time-weighted average exposures have been determined so that the carboxyhaemoglobin level of 2.5% is not exceeded, even when a normal subject engages in relatively heavy work.

Cigarette consumption represents a special case of carbon monoxide exposure; for the smoker, it almost always dominates over personal exposure from other sources. Studies by Radford & Drizd (1982) show that carboxyhaemoglobin levels of cigarette smokers average 4%, whereas those of non-smokers average 1%. Therefore, this summary focuses on environmental exposure of non-smokers to carbon monoxide.

People encounter carbon monoxide in a variety of environments — while travelling in motor vehicles, working at their jobs, visiting urban locations associated with combustion sources, or cooking and heating with domestic gas, charcoal or wood fires — as well as in tobacco smoke. Studies of human exposure have shown that among these settings, the motor vehicle is the most important for regularly encountered elevations of carbon monoxide. Studies conducted by the US EPA in Denver, Colorado, and Washington, DC, for example, have demonstrated that the motor vehicle interior has the highest average carbon monoxide concentrations (averaging 8–11 mg/m$^3$ [7–10 ppm]) of all microenvironments (Johnson, 1984).
Another important setting for carbon monoxide exposure is the workplace. In general, carbon monoxide exposures at work exceed exposures during non-work periods, apart from commuting to and from work. Average concentrations may be elevated during this period because workplaces are often located in congested areas that have higher background carbon monoxide concentrations than do many residential neighbourhoods. Occupational and non-occupational exposures may overlay one another and result in a higher concentration of carbon monoxide in the blood. Certain occupations also increase the risk of high carbon monoxide exposure. These include those occupations involved directly with vehicle driving, maintenance and parking, such as auto mechanics; parking garage and gas station attendants; bus, truck or taxi drivers; traffic police; and warehouse workers. Some industrial processes produce carbon monoxide directly or as a by-product, including steel production, nickel refining, coke ovens, carbon black production and petroleum refining. Firefighters, cooks and construction workers may also be exposed to higher carbon monoxide levels at work. Occupational exposures in industries or settings with carbon monoxide production also represent some of the highest individual exposures observed in field monitoring studies.

The highest indoor non-occupational carbon monoxide exposures are associated with combustion sources and include enclosed parking garages, service stations and restaurants. The lowest indoor carbon monoxide concentrations are found in homes, churches and health care facilities. The US EPA’s Denver Personal Monitoring Study showed that passive cigarette smoke is associated with increasing a non-smoker’s exposure by an average of about 1.7 mg/m$^3$ (1.5 ppm) and that use of a gas range is associated with an increase of about 2.9 mg/m$^3$ (2.5 ppm) at home. Other sources that may contribute to higher carbon monoxide levels in the home include combustion space heaters and wood- and coal-burning stoves.

5.2 Population exposure to carbon monoxide

5.2.1 Ambient air monitoring

Many early attempts to estimate exposure of human populations used data on ambient air quality from fixed monitoring stations. An example of such an analysis can be found in the 1980 annual report of the President’s Council on Environmental Quality (1980). In this
analysis, a county’s exposure to an air pollutant was estimated as the product of the number of days on which violations of the primary standard were observed at county monitoring sites multiplied by the county’s population. Exposure was expressed in units of person-days. National exposure to an air pollutant was estimated by the sum of all county exposures.

The methodology employed by the Council on Environmental Quality provides a relatively crude estimate of exposure and is limited by four assumptions:

(1) The exposed populations do not travel outside areas represented by fixed-site monitors.

(2) The air pollutant concentrations measured with the network of fixed-site monitors are representative of the concentrations breathed by the population throughout the area.

(3) The air quality in any one area is only as good as that at the location that has the worst air quality.

(4) There are no violations in areas of the county that are not monitored.

Many studies cast doubt on the validity of these assumptions for carbon monoxide. These studies are reviewed in Ott (1982) and in Spengler & Soczek (1984). Doubts over the ability of fixed-site monitors alone to accurately depict air pollutant exposures are based on two major findings on fixed-site monitor representativeness:

(1) Indoor and in-transit concentrations of carbon monoxide may be significantly different from ambient carbon monoxide concentrations.

(2) Ambient outdoor concentrations of carbon monoxide with which people come in contact may vary significantly from carbon monoxide concentrations measured at fixed-site monitors.

In estimating exposure, the Council on Environmental Quality also assumed that each person in the population spends 24 h at home.
This assumption permitted the use of readily available demographic data from the US Bureau of the Census. Data collected 20 years ago indicate that people spend a substantial portion of their time away from home. In a study of metropolitan Washington, DC, residents during 1968, Chapin (1974) found that people spent an average 6.3 h away from home on Sunday and 10.6 h away from home on Friday. This translates to between 26.3% and 44.2% of the day spent away from home. More recent personal exposure and time budget studies (e.g., Johnson, 1987; Schwab et al., 1990) also indicate that a substantial portion of time is spent away from home.

Fixed-site monitors measure concentrations of pollutants in ambient air. Ambient air has been defined by the US EPA in the Code of Federal Regulations (OSHA, 1991b) as air that is “external to buildings, to which the general public has access.” But the nature of modern urban lifestyles in many countries, including the USA, indicates that people spend an average of over 20 h per day indoors (Meyer, 1983). Reviews of studies on this subject by Yocom (1982), Meyer (1983) and Spengler & Soczek (1984) show that measurements of indoor carbon monoxide concentrations vary significantly from simultaneous measurements in ambient air. The difference between indoor and outdoor air quality and the amount of time people spend indoors reinforce the conclusion that using ambient air quality measurements alone will not provide accurate estimates of population exposure.

5.2.2 Approaches for estimating population exposure

In recent years, researchers have focused on the problem of determining actual population exposures to carbon monoxide. There are three alternative approaches for estimating the exposures of a population to air pollution: the “direct approach,” using field measurement of a representative population carrying PEMs; the “indirect approach,” involving computation from field data of activity patterns and measured concentration levels within microenvironments (Ott, 1982); and a hybrid approach that combines the direct and indirect approaches (Mage, 1991).

In the direct approach, as study participants engage in regular daily activities, they are responsible for recording their exposures to the pollutant of interest using a personal monitor. Subjects can record their exposures in a diary, the method used in a US pilot study in
Los Angeles, California (Ziskind et al., 1982), or they can automatically store exposure data in a data logger, the method used in studies in Denver, Colorado (Johnson, 1984), and Washington, DC (Hartwell et al., 1984), which are summarized by Akland et al. (1985). In all of these studies, subjects also recorded the time and nature of their activities while they monitored personal exposures to carbon monoxide.

The direct approach can be used to obtain an exposure inventory of a representative sample from either the general population or a specific subpopulation, which can be defined by many demographic, occupational and health factors. The inventory can cover a range of microenvironments encountered over a period of interest (e.g., a day), or it can focus on one particular microenvironment. With this flexibility, policy analysts can assess the problem that emission sources pose to a particular subgroup (e.g., commuters) active in a specific microenvironment (e.g., automobiles).

The indirect approach to estimating personal exposure is to use PEMs or microenvironmental monitors to monitor microenvironments rather than individuals. Combined with the ambient data and additional data on human activities that occur in these microenvironments, data from the indirect approach can be used to estimate the percentage of a subpopulation that is at risk for exposure to pollutant concentrations that exceed national or regional air quality standards. Flachsbart & Brown (1989) conducted this type of study to estimate merchant exposure to carbon monoxide from motor vehicle exhaust at the Ala Moana Shopping Center in Honolulu, Hawaii, USA.

### 5.2.3 Personal monitoring field studies

The development of small PEMs made possible the large-scale carbon monoxide human exposure field studies in Denver, Colorado, and Washington, DC, in the winter of 1982–83 (Aklad et al., 1985). These monitors proved effective in generating 24-h carbon monoxide exposure profiles on 450 persons in Denver and 800 persons in Washington, DC. The Denver–Washington, DC, study is the only large-scale field study on population exposure to carbon monoxide that has been undertaken to date.

Results from the Denver–Washington, DC, study (Aklad et al., 1985) show that over 10% of the Denver residents and 4% of the
Washington, DC, residents were exposed to 8-h average carbon monoxide levels above 10 mg/m$^3$ (9 ppm) during the winter study period. This degree of population exposure could not be accurately deduced from simultaneous data collected by the fixed-site monitors without taking into account other factors, such as contributions from indoor sources, elevated levels within vehicles and individuals’ activity patterns. In Denver, for example, the fixed-site monitors exceeded the 10 mg/m$^3$ (9 ppm) level only 3.1% of the time. These results indicate that the effects of personal activity, indoor sources and, especially, time spent commuting all greatly contribute to a person’s carbon monoxide exposure.

This study emphasizes that additional strategies are required to augment data from fixed-site monitoring networks in order to evaluate actual human carbon monoxide exposures and health risks within a community. The cumulative carbon monoxide data for both Denver and Washington, DC, show that personal monitors often measure higher concentrations than do fixed stations. As part of this study, 1-h exposures to carbon monoxide concentrations as determined by personal monitors were compared with measured ambient concentrations at fixed monitor sites. Correlations between personal monitor data and fixed-site data were consistently poor; the fixed-site data usually explained less than 10% of the observed variation in personal exposure. For example, 1-h carbon monoxide measurements taken at the nearest fixed stations were only weakly correlated (0.14 $r$ 0.27) with office or residential measurements taken with personal monitors (Akland et al., 1985).

The conclusion that exposure of persons to ambient carbon monoxide and other pollutants does not directly correlate with concentrations determined at fixed-site monitors is supported by the work of others (Ott & Eliassen, 1973; Cortese & Spengler, 1976; Dockery & Spengler, 1981; Wallace & Ott, 1982; Wallace & Ziegenfus, 1985). Results from the Finnish Liila study in Helsinki, in which personal carbon monoxide and nitrogen dioxide exposures of preschool children were monitored, showed that their short-term personal carbon monoxide exposures did not correlate with carbon monoxide levels in ambient air and that gas stove use at home was the dominant determinant of carbon monoxide exposure (Alm et al., 1994).
In view of the high degree of variability of ambient carbon monoxide concentrations over both space and time and the presence of indoor sources of carbon monoxide, the reported results are not surprising. A given fixed monitor is unable to track the exposure of individuals to ambient carbon monoxide as they go about their daily activities, moving from one location to another, all of which are seldom in the immediate vicinity of the monitor. This does not necessarily mean, however, that fixed monitors do not give some useful general information on the overall level of exposure of a population to carbon monoxide. The Denver and Washington, DC, data, although failing to show a correlation between exposures measured by individual personal monitors and simultaneous concentrations measured by the nearest fixed-site monitors, did suggest that, in Denver, aggregate personal exposures were lower on days of lower ambient carbon monoxide levels as determined by fixed-site monitors and higher on days of higher ambient levels. Also, both fixed-site and personal exposures were higher in Denver than in Washington, DC. For example, the median ambient daily 1-h maximum carbon monoxide concentration was measured by fixed monitors to be 3.7 mg/m$^3$ (3.2 ppm) higher in Denver than in Washington, DC, and the personal median daily 1-h maximum carbon monoxide exposure was measured by PEMs to be 4.5 mg/m$^3$ (3.9 ppm) higher in Denver. Likewise, the median ambient daily 8-h maximum carbon monoxide concentration measured by fixed monitors was found to be 3.3 mg/m$^3$ (2.9 ppm) higher in Denver, whereas the personal median daily 8-h maximum carbon monoxide exposure was 3.9 mg/m$^3$ (3.4 ppm) higher in Denver.

The in-transit microenvironment with the highest estimated carbon monoxide concentration was the motorcycle, whereas walking and bicycling had the lowest carbon monoxide concentrations. Outdoor microenvironments can also be ranked for these data. Outdoor public garages and outdoor residential garages and carports had the highest carbon monoxide concentrations; outdoor service stations, vehicle repair facilities and parking lots had intermediate concentrations. In contrast, school grounds and residential grounds had relatively low concentrations, whereas extremely low carbon monoxide concentrations were found in outdoor sports arenas, amphitheatres, parks and golf courses. Finally, a wide range of concentrations was found in Denver within indoor microenvironments. The highest indoor carbon monoxide
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concentrations occurred in service stations, vehicle repair facilities and public parking garages; intermediate concentrations were found in shopping malls, residential garages, restaurants, offices, auditoriums, sports arenas, concert halls and stores; and the lowest concentrations were found in health care facilities, public buildings, manufacturing facilities, homes, schools and churches.

One activity that influences personal exposure is commuting. An estimated 1% of the non-commuters in Washington, DC, were exposed to concentrations above 10 mg/m$^3$ (9 ppm) for 8 h. By comparison, an estimated 8% of persons reporting that they commuted more than 16 h per week had 8-h carbon monoxide exposures above the 10 mg/m$^3$ (9 ppm) level. Finally, certain occupational groups whose work brings them in close proximity to the internal combustion engine had a potential for elevated carbon monoxide exposures. These include automobile mechanics; parking garage or gas station attendants; crane deck operators; cooks; taxi, bus and truck drivers; firemen; policemen; and warehouse and construction workers. Of the 712 carbon monoxide exposure profiles obtained in Washington, DC, 29 persons fell into this “high-exposure” category. Of these, 25% had 8-h carbon monoxide exposures above the 10 mg/m$^3$ (9 ppm) level.

Several field studies have also been conducted by the US EPA to determine the feasibility and effectiveness of monitoring selected microenvironments for use in estimating exposure profiles indirectly. One study (Flachsbart et al., 1987), conducted in Washington, DC, in 1982 and 1983, concentrated on the commuting microenvironment, because earlier studies identified this microenvironment type as the single most important non-occupational microenvironment relative to total carbon monoxide population exposure. It was observed that for the typical automobile commuter, the time-weighted average carbon monoxide exposure while commuting ranged from 10 to 16 mg/m$^3$ (9 to 14 ppm). The corresponding rush-hour (7:00 to 9:00 a.m., 4:00 to 6:00 p.m.) averages at fixed-site monitors were 3.1–3.5 mg/m$^3$ (2.7–3.1 ppm).

5.2.4 Carbon monoxide exposures indoors

People in developed countries spend a majority (~85%) of their time indoors (US EPA, 1989a,b); therefore, a comprehensive depiction of exposure to carbon monoxide must include this setting. The indoor sources, emissions and concentrations are sufficiently diverse, however, that only a few studies can be cited here as
examples. Targeted field studies that have monitored indoor carbon monoxide levels as a function of the presence or absence of combustion sources are described in more detail in section 5.6.

Early studies date back to before 1970, when it was found that indoor and outdoor carbon monoxide levels do not necessarily agree. For example, one study determined indoor–outdoor relationships for carbon monoxide over 2-week periods during summer, winter and fall in 1969 and 1970 in buildings in Hartford, Connecticut, USA (Yocom et al., 1971). With the exception of the private homes, which were essentially equal, there was a day-to-night effect in the fall and winter seasons; days were higher by about a factor of 2. These differences are consistent with higher traffic-related carbon monoxide levels outdoors in the daytime.

Indoor and outdoor carbon monoxide concentrations were measured in four homes, also in the Hartford, Connecticut, area, in 1973 and 1974 (Wade et al., 1975). All used gas-fired cooking stoves. Concentrations were measured in the kitchen, living room and bedroom. Stove use, as determined by activity diaries, correlated directly with carbon monoxide concentrations. Peak carbon monoxide concentrations in several of the kitchens exceeded 10 mg/m$^3$ (9 ppm), but average concentrations ranged from 2.3–3.4 mg/m$^3$ (2–3 ppm) to about 9 mg/m$^3$ (8 ppm). These results are in general agreement with results obtained in Boston, Massachusetts, USA (Moschandreas & Zabransky, 1982). In this study, the investigators found significant differences between carbon monoxide concentrations in rooms in homes where there were gas appliances.

Effects of portable kerosene-fired space heaters on indoor air quality were measured in an environmental chamber and a house (Traynor et al., 1982). Carbon monoxide emissions from white flame and blue flame heaters were compared. The white flame convective heater emitted less carbon monoxide than the blue flame radiant heater. Concentrations in the residence were <2.3 mg/m$^3$ (<2 ppm) and 2.3–8 mg/m$^3$ (2–7 ppm), respectively. The authors concluded that high levels might occur when kerosene heaters are used in small spaces or when air exchange rates are low.

A rapid method using an electrochemical PEM to survey carbon monoxide was applied in nine high-rise buildings in the San
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Francisco and Los Angeles, California, areas during 1980 and 1984 (Flachsbart & Ott, 1986). One building had exceptionally high carbon monoxide levels compared with the other buildings; average concentrations on various floors ranged from 6 to 41 mg/m$^3$ (5 to 36 ppm). The highest levels were in the underground parking garage, which was found to be the source of elevated carbon monoxide within the building through transport via the elevator shaft.

The effect of residential wood combustion and specific heater type on indoor carbon monoxide levels has been investigated (Humphreys et al., 1986). Airtight and non-airtight heaters were compared in a research home in Tennessee, USA. Carbon monoxide emissions from the non-airtight heaters were generally higher than those from the airtight heaters. Peak indoor carbon monoxide concentration (ranging from 1.5 to 33.9 mg/m$^3$ [1.3 to 29.6 ppm], depending on heater type) was related to fuel reloadings.

Two studies in the Netherlands have measured carbon monoxide levels in homes. Carbon monoxide levels in 254 Netherland homes with unvented gas-fired geysers (water heaters) were investigated during the winter of 1980 (Brunekreef et al., 1982). Concentrations at breathing height were grouped into the following categories: $\#1$ mg/m$^3$ (0 ppm; $n = 154$), $\#2$–$\#11$ mg/m$^3$ (11–50 ppm; $n = 50$), $\#12$–$\#15$ mg/m$^3$ (51–100 ppm; $n = 25$) and $\#16$ mg/m$^3$ (>100 ppm; $n = 17$). They found that a heater vent reduced indoor carbon monoxide concentrations and that the type of burner affected carbon monoxide levels. In another study, air pollution in Dutch homes was investigated by Lebret (1985). Carbon monoxide concentrations were measured in the kitchen (0–20.0 mg/m$^3$ [0–17.5 ppm]), the living room (0–10.0 mg/m$^3$ [0–8.7 ppm]) and the bedroom (0–4.0 mg/m$^3$ [0–3.5 ppm]). Carbon monoxide levels were elevated in homes with gas cookers and unvented geysers. Kitchen carbon monoxide levels were higher than those in other locations as a result of peaks from the use of gas appliances. Carbon monoxide levels in living rooms were slightly higher in houses with smokers. The overall mean carbon monoxide level indoors was 0–3.1 mg/m$^3$ (0–2.7 ppm) above outdoor levels.

In Zagreb, Yugoslavia, carbon monoxide was measured in eight urban institutions housing sensitive populations, including kindergartens, a children’s hospital and homes for the elderly (Sisovic &
Fugas, 1985). Winter carbon monoxide concentrations ranged from 1.3 to 15.7 mg/m³ (1.1 to 13.7 ppm), and summer concentrations ranged from 0.7 to 7.9 mg/m³ (0.6 to 6.9 ppm). The authors attributed indoor carbon monoxide concentrations to nearby traffic density, general urban pollution, seasonal differences and day-to-day weather conditions. Indoor sources were not reported.

Toxic levels of carbon monoxide were also found in measurements at six ice skating rinks (Johnson et al., 1975b). This study was prompted by the reporting of symptoms of headache and nausea among 15 children who patronized one of the rinks. Carbon monoxide concentrations were found to be as high as 350 mg/m³ (304 ppm) during operation of a propane-powered ice-resurfacing machine. Depending on skating activity levels, the ice-resurfacing operation was performed for 10 min every 1–2 h. Because this machine was found to be the main source of carbon monoxide, using catalytic converters and properly tuning the engine greatly reduced emissions of carbon monoxide and, hence, reduced carbon monoxide concentrations. Similar findings have been reported by Spengler et al. (1978), Lévesque et al. (1990), Paulozzi et al. (1993) and Lee et al. (1994).

5.2.5 Carbon monoxide exposures inside vehicles

Studies of carbon monoxide concentrations inside automobiles have also been reported over the past decade.

Petersen & Sabersky (1975) measured pollutants inside an automobile under typical driving conditions. Carbon monoxide concentrations were generally less than 29 mg/m³ (25 ppm), with one 3-min peak of 52 mg/m³ (45 ppm). Average concentrations inside the vehicle were similar to those outside. No in-vehicle carbon monoxide sources were noted; however, a commuter’s exposure is usually determined by other high-emitting vehicles, not by the driven vehicle itself (Chan et al., 1989; Shikiya et al., 1989).

Drowsiness, headache and nausea were reported by eight children who had ridden in school buses for about 2 h while travelling on a ski trip (Johnson et al., 1975a). The students reporting symptoms were seated in the rear of the bus, which had a rear-mounted engine and a leaky exhaust. The exhaust system was subsequently repaired. During a later ski outing for students, carbon monoxide concentrations were also monitored for a group of 66 school buses in
the parking lot. The investigators found 5 buses with carbon monoxide concentrations of 6–29 mg/m$^3$ (5–25 ppm) (mean 17 mg/m$^3$ (15 ppm)), 24 buses showing concentrations in excess of 10 mg/m$^3$ (9 ppm) for short periods and 2 buses showing up to 3 times the 10 mg/m$^3$ (9 ppm) level for short periods. Drivers were advised to park so that exhausts from one bus would not be adjacent to the fresh air intake for another bus.

During a US cross-country trip in the spring of 1977, Chaney (1978) measured in-vehicle carbon monoxide concentrations. The carbon monoxide levels varied depending on traffic speed. On expressways in Chicago, Illinois, San Diego, California, and Los Angeles, California, when traffic speed was less than 16 km/h, carbon monoxide concentrations exceeded 17 mg/m$^3$ (15 ppm). Levels increased to 52 mg/m$^3$ (45 ppm) when traffic stopped. In addition, it was observed that heavily loaded vehicles (e.g., trucks) produced high carbon monoxide concentrations inside nearby vehicles, especially when the trucks were ascending a grade.

Colwill & Hickman (1980) measured carbon monoxide concentrations in 11 new cars as they were driven on a heavily trafficked route in and around London, United Kingdom. The inside mean carbon monoxide level for the 11 cars was 28.9 mg/m$^3$ (25.2 ppm), whereas the outside mean level was 53.8 mg/m$^3$ (47.0 ppm).

In a study mandated by the US Congress in the 1977 Clean Air Act Amendments, the EPA studied carbon monoxide intrusion into vehicles (Ziskind et al., 1981). The objective was to determine whether carbon monoxide was leaking into the passenger compartments of school buses, police cars and taxis and, if so, how prevalent the situation was. The study involved 1164 vehicles in Boston, Massachusetts, and Denver, Colorado. All vehicles were in use in a working fleet at the time of testing. The results indicated that all three types of vehicles often have multiple (an average of four to five) points of carbon monoxide intrusion — worn gaskets, accelerator pedals, rust spots in the trunk, etc. In 58% of the rides lasting longer than 8 h, carbon monoxide levels exceeded 10 mg/m$^3$ (9 ppm). Thus, the study provided evidence that maintenance and possibly design of vehicles may be important factors in human exposure to carbon monoxide.
Petersen & Allen (1982) reported the results of carbon monoxide measurements taken inside vehicles under typical driving conditions in Los Angeles, California, over 5 days in October 1979. They found that the average ratio of interior to exterior carbon monoxide concentrations was 0.92. However, the hourly average interior carbon monoxide concentrations were 3.9 times higher than the nearest fixed-site measurements. In their analysis of the factors that influence interior carbon monoxide levels, they observed that traffic flow and traffic congestion (stop-and-go) are important, but “comfort state” (i.e., car windows open/closed, fan on/off, etc.) and meteorological parameters (i.e., wind speed, wind direction) have little influence on incremental exposures. Another study, carried out in Paris, France (Dor et al., 1995), also showed that the carbon monoxide concentration in cars can be 3 times that of the ambient air. A study in Hong Kong showed that the same may be true for concentrations in buses (Chan & Wu, 1993).

Flachsbart (1989) investigated the effectiveness of priority lanes on a Honolulu, Hawaii, arterial highway in reducing commuter travel time and exposure to carbon monoxide. The carbon monoxide concentrations and exposures of commuters in these lanes were substantially lower than in the non-priority lanes. Carbon monoxide exposure was reduced approximately 61% for express buses, 28% for high-occupancy vehicles and 18% for carpools when compared with that for regular automobiles. The higher speed associated with priority lanes helped reduce carbon monoxide exposure. These observations demonstrate that carbon monoxide concentrations have a high degree of spatial variability on roadways, associated with vehicle speed and traffic volume.

Ott et al. (1994) measured carbon monoxide exposures inside a car travelling on a major urban arterial highway in El Camino Real in the USA (traffic volume 30 500–45 000 vehicles per day) over a 13.5-month period. For 88 trips, the mean carbon monoxide concentration was 11.2 mg/m³ (9.8 ppm), with a standard deviation of 6.6 mg/m³ (5.8 ppm).

Fernadenz-Bremauntz & Ashmore (1995a,b) related exposure of commuters in vehicles to carbon monoxide to fixed-site concentrations at monitoring stations in Mexico City. The ambient levels were all more than 15 mg/m³ (13 ppm). The highest median
and 90th percentile in-vehicle concentrations were found in autos and minibuses (49–68 and 77–96 mg/m³ [43–59 and 67–84 ppm]), with lower levels in buses (34 and 49 mg/m³ [30 and 43 ppm]), trolleys (30 and 44 mg/m³ [26 and 38 ppm]) and metro and light rail (24 and 33 mg/m³ [21 and 29 ppm]). Average in-vehicle/ambient ratios for each mode of transport were as follows: automobile, 5.2; minivan, 5.2; minibus, 4.3; bus, 3.1; trolleybus, 3.0; and metro, 2.2.

Chan et al. (1991) investigated driver exposure to volatile organic chemicals, carbon monoxide, ozone and nitrogen dioxide under different urban, rural and interstate highway driving conditions using four different cars in Raleigh, North Carolina, USA. They found that the in-vehicle carbon monoxide concentrations did not vary significantly between the cars, and they were on average 4.5 times higher than the ambient carbon monoxide measurements. Car ventilation had little effect on the driver exposures.

Two Finnish studies of personal air pollution exposures of children showed that preschool children who commuted to a day care centre by bus or car were exposed to considerably higher peak carbon monoxide levels than children who went to the day care centre by walking or on a bike (Jantunen et al., 1995) and that the average carbon monoxide exposure of schoolchildren in Kuopio, Finland, in a car or bus was 4 times higher than in other microenvironments (Alm et al., 1995).

### 5.2.6 Carbon monoxide exposures outdoors

Carbon monoxide concentrations in outdoor settings (besides those measured at fixed monitoring stations) show considerable variability. Ott (1971) made 1128 carbon monoxide measurements at outdoor locations in San Jose, California, USA, at breathing height over a 6-month period and compared these results with the official fixed monitoring station data. This study simulated the measurements of the outdoor carbon monoxide exposures of pedestrians in downtown San Jose by having them carry personal monitoring pumps and sampling bags while walking standardized routes on congested sidewalks. If an outdoor measurement was made more than 100 m away from any major street, its carbon monoxide concentration was similar, suggesting the existence of a generalized urban background concentration in San Jose that was spatially uniform over the city (within a 33-km² grid) when one is sufficiently far away from mobile...
sources. Because the San Jose monitoring station was located near a street with heavy traffic, it recorded concentrations approximately 100% higher than this background value. In contrast, outdoor carbon monoxide levels from personal monitoring studies of downtown pedestrians were 60% above the corresponding monitoring station values, and the correlation coefficient was low \((r = 0.20)\). By collecting the pedestrian personal exposures over 8-h periods, it was possible to compare the levels with the air quality standards. On 2 of 7 days for which data were available, the pedestrian concentrations were particularly high \((15 \text{ and } 16.3 \text{ mg/m}^3 [13 \text{ and } 14.2 \text{ ppm}])\) and were 2–3 times the corresponding levels recorded at the same time \((5.0 \text{ and } 7.1 \text{ mg/m}^3 [4.4 \text{ and } 6.2 \text{ ppm}])\) at the air monitoring station \((\text{Ott} \& \text{Eliassen, 1973; Ott} \& \text{Mage, 1975})\). These results show that concentrations to which pedestrians were exposed on downtown streets could exceed recommended air quality standards, although the official air monitoring station record values were significantly less than that. It can be argued, however, that not many pedestrians spend a lot of time outdoors walking along downtown sidewalks, and that is one of the important reasons for including realistic human activity patterns in exposure assessments. It should also be noted that street-level carbon monoxide concentrations have significantly decreased over the last decade in countries where vehicular emission controls are in place.

Godin et al. (1972) conducted similar studies in downtown Toronto, Ontario, Canada, using 100-ml glass syringes in conjunction with NDIR spectrometry. They measured carbon monoxide concentrations along streets, inside passenger vehicles and at a variety of other locations. Like other investigators, they found that carbon monoxide concentrations were determined by very localized phenomena. In general, carbon monoxide concentrations in traffic and along streets were much higher than those observed at conventional fixed air monitoring stations. In a subsequent study in Toronto, Wright et al. (1975) used Ecolyzers to measure 4- to 6-min average carbon monoxide concentrations encountered by pedestrians and street workers and obtained similar results. Levels ranged from 11 to 57 mg/m³ (10 to 50 ppm), varying with wind speed and direction, atmospheric stability, traffic density and height of buildings. They also measured carbon monoxide concentrations on the sidewalks of a street that subsequently was closed to traffic to become a pedestrian mall. Before the street was closed, the average concentrations at two intersections were \(10.8 \pm 4.6 \text{ mg/m}^3 (9.4 \pm 4.0 \text{ ppm})\) and \(9.0 \pm 2.2 \text{ mg/m}^3 (7.9 \pm\)
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1.9 ppm) (mean, plus or minus standard deviation); after the street was closed, the averages dropped to 4.2 ± 0.6 mg/m³ (3.7 ± 0.5 ppm) and 4.6 ± 1.1 mg/m³ (4.0 ± 1.0 ppm), respectively, which were equivalent to the background level.

A large-scale field investigation was undertaken of carbon monoxide concentrations in indoor and outdoor locations in five California, USA, cities using personal monitors (Ott & Flachsbart, 1982). For outdoor commercial settings, the average carbon monoxide concentration was 5 mg/m³ (4 ppm). This carbon monoxide level was statistically, but not substantially, greater than the average carbon monoxide concentration of 2.3 mg/m³ (2 ppm) recorded simultaneously at nearby fixed monitoring stations.

The Organisation for Economic Co-operation and Development (OECD, 1997) recently published a study of trends and relative concentrations in Western Europe, the USA and Japan between 1988 and 1993, based on the annual maximum 8-h average concentration at urban traffic and urban residential sites. This showed that the average levels remained unchanged, but, at the most polluted locations in both residential and commercial (heavily trafficked) areas, levels of carbon monoxide have declined significantly. A short summary of results of different countries is given in Table 6, as published by the OECD (1997). Carbon monoxide measurements in atmospheric air were performed in many countries — for example, at approximately 300 sites in Germany using automatic devices.

Investigations in traffic routes of Amsterdam, Netherlands (van Wijnen et al., 1995), using personal air sampling resulted in much higher carbon monoxide concentrations in the samples of car drivers than in the personal air samples of cyclists. Similar results from Germany were cited.

5.3 Estimating population exposure to carbon monoxide

Accurate estimates of human exposure to carbon monoxide are a prerequisite for both a realistic appraisal of the risks posed by the pollutant and the design and implementation of effective control strategies. This section discusses the general concepts on which exposure assessment is based and approaches for estimating population exposure to carbon monoxide using exposure models. Because
Table 6. Comparison of carbon monoxide concentrations, 1993

<table>
<thead>
<tr>
<th>Site</th>
<th>Averaging period</th>
<th>Statistic</th>
<th>Western Europe</th>
<th>USA</th>
<th>Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carbon monoxide concentration</td>
<td>mg/m³</td>
<td>ppm</td>
<td>mg/m³</td>
</tr>
<tr>
<td>Urban traffic</td>
<td>8-h average</td>
<td>Average</td>
<td>8.3</td>
<td>7.2</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>8-h average</td>
<td>95th percentile</td>
<td>13.1</td>
<td>11.4</td>
<td>11.6</td>
</tr>
<tr>
<td>Urban residential</td>
<td>8-h average</td>
<td>Average</td>
<td>5.7</td>
<td>5</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>8-h average</td>
<td>95th percentile</td>
<td>9.5</td>
<td>8.3</td>
<td>10.1</td>
</tr>
</tbody>
</table>
of problems in estimating population exposure solely from fixed-station data, several formal human exposure models have been developed. Some of these models include information on human activity patterns: the microenvironments people visit and the times they spend there. These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor and in-transit settings.

### 5.3.1 Components of exposure

Two aspects of exposure bear directly on the related health consequences. The first is the magnitude of the pollutant exposure. The second is the duration of the exposure. The magnitude is an important exposure parameter, because concentration typically is assumed to be directly proportional to dose and, ultimately, to the health outcome. But exposure implies a time component, and it is essential to specify the duration of an exposure. The health risks of exposure to a specific concentration for 5 min are likely to be different, all other factors being equal, from those of exposure to the same concentration for an hour.

The magnitude and duration of exposure can be determined by plotting an individual’s air pollution exposure over time. The function $C_i(t)$ describes the air pollutant concentration to which an individual is exposed at any point in time $t$. Ott (1982) defined the quantity $C_i(t)$ as the *instantaneous exposure* of an individual. The shaded area under the graph represents the accumulation of instantaneous exposures over some period of time ($t_f - t_i$). This area is also equal to the integral of the air pollutant concentration function, $C_i(t)$, between $t_i$ and $t_f$. Ott (1982) defined the quantity represented by this area as the *integrated exposure*.

The average exposure, calculated by dividing the integrated exposure by the period of integration ($t_f - t_i$), represents the average air pollutant concentration to which an individual was exposed over the defined period of exposure. To facilitate comparison with established air quality standards, an averaging period is usually chosen to equal the averaging period of the standard. In this case, the average exposure is referred to as a standardized exposure.

As discussed above, exposure represents the joint occurrence of an individual being located at point $(x,y,z)$ during time $t$ with the
The simultaneous presence of an air pollutant at concentration $C_{\text{xyz}}(t)$. Consequently, an individual’s exposure to an air pollutant is a function of location as well as time. If a volume at a location can be defined such that air pollutant concentrations within it are relatively homogeneous, yet potentially different from other locations, the volume may be considered a “microenvironment” (Duan, 1982). Microenvironments may be aggregated by location (e.g., indoor or outdoor) or activity performed at a location (e.g., residential or commercial) to form microenvironment types.

It is important to distinguish between individual exposures and population exposures. Sexton & Ryan (1988) defined the pollutant concentrations experienced by a specific individual during normal daily activities as “personal” or “individual” exposures. A personal exposure depends on the air pollutant concentrations that are present in the locations through which the person moves, as well as on the time spent at each location. Because time–activity patterns can vary substantially from person to person, individual exposures exhibit wide variability (Dockery & Spengler, 1981; Quackenboss et al., 1982; Sexton et al., 1984; Spengler et al., 1985; Stock et al., 1985; Wallace et al., 1985). Thus, although it is a relatively straightforward procedure to measure any one person’s exposure, many such measurements may be needed to quantify the mean and variance of exposures for a defined group. The daily activities of a person in time and space define his or her activity pattern. Accurate estimates of air pollution exposure generally require that an exposure model account for the activity patterns of the population of interest. The activity patterns may be determined through “time budget” studies of the population. Studies of this type have been performed by Szalai (1972), Chapin (1974), Michelson & Reed (1975), Robinson (1977), Johnson (1987) and Schwab et al. (1990). The earlier studies may now be out of date because they were not designed to investigate human exposure questions and because lifestyles have changed over the past 25 years. Ongoing exposure studies have adopted the diary methods that were developed for sociological investigations and applied them to current exposure and time budget investigations. A few of these studies have been reported (e.g., Johnson, 1987; Schwab et al., 1990).

From a public health perspective, it is important to determine the “population exposure;” which is the aggregate exposure for a specified group of people (e.g., a community or an identified occupational
cohort). Because exposures are likely to vary substantially between individuals, specification of the distribution of personal exposures within a population, including the average value and the associated variance, is often the focus of exposure assessment studies. The upper tail of the distribution, which represents those individuals exposed to the highest concentrations, is frequently of special interest, because the determination of the number of individuals who experience elevated pollutant levels can be critical for health risk assessments. This is especially true for pollutants for which the relationship between dose and response is highly non-linear.

5.3.2 Approaches to exposure modelling

In recent years, the limitations of using fixed-site monitors alone to estimate public exposure to air pollutants have stimulated interest in using portable monitors to measure personal exposure. These PEMs were developed for carbon monoxide in the late 1970s by Energetics Science Incorporated and by General Electric. Wallace & Ott (1982) surveyed PEMs available then for carbon monoxide and other air pollutants.

The availability of these monitors has facilitated use of the direct and indirect approaches to assessing personal exposure (see section 5.2.2). Whether the direct or indirect approach is followed, the estimation of population exposure requires a “model” — that is, a mathematical or computerized approach of some kind. Sexton & Ryan (1988) suggested that most exposure models can be classified as one of three types: statistical, physical or physical-stochastic.

The statistical approach requires the collection of data on human exposures and the factors thought to be determinants of exposure. These data are combined in a statistical model, normally a regression equation or an analysis of variance, to investigate the relationship between air pollution exposure (dependent variable) and the factors contributing to the measured exposure (independent variables). An example of a statistical model is the regression model developed by Johnson et al. (1986) for estimating carbon monoxide exposures in Denver, Colorado, based on data obtained from the Denver Personal Monitoring Study. If the study group constitutes a representative sample, the derived statistical model may be extrapolated to the population defined by the sampling frame. It should also be noted that selection of factors thought to influence exposure has a substantial
effect on the outcome of the analysis. Spurious conclusions can be
drawn, for example, from statistical models that include parameters
that are correlated with, but not causally related to, air pollution
exposure.

In the physical modelling approach, the investigator makes an
\textit{a priori} assumption about the underlying physical processes that
determine air pollution exposure and then attempts to approximate
these processes through a mathematical formulation. Because the
model is chosen by the investigator, it may produce biased results
because of the inadvertent inclusion of inappropriate parameters or
the improper exclusion of critical components. The National Ambient
Air Quality Standards (NAAQS) Exposure Model as originally
applied to carbon monoxide by Johnson & Paul (1983) is an example
of a physical model.

The physical-stochastic approach combines elements of both the
physical and statistical modelling approaches. The investigator begins
by constructing a mathematical model that describes the physical
basis for air pollution exposure. Then, a random or stochastic
component that takes into account the imperfect knowledge of the
physical parameters that determine exposure is introduced into the
model. The physical-stochastic approach limits the effect of
investigator-induced bias by the inclusion of the random component
and allows for estimates of population distributions for air pollution
exposure. Misleading results may still be produced, however, because
of poor selection of model parameters. In addition, the required
knowledge about distributional characteristics may be difficult to
obtain. Examples of models based on this approach that have been
applied to carbon monoxide include the Simulation of Human Activity
and Pollutant Exposure model (Ott, 1984; Ott et al., 1988) and two
models derived from the NAAQS Exposure Model, developed by
Johnson et al. (1990).

5.4 Exposure measurements in populations and
subpopulations

5.4.1 \textit{Carboxyhaemoglobin measurements in populations}

Numerous studies have used the above-described methodologies
to characterize the levels of carboxyhaemoglobin in the general
population. These studies have been designed to determine frequency distributions of carboxyhaemoglobin levels in the populations being studied. In general, the higher the frequency of carboxyhaemoglobin levels above baseline in non-smoking subjects, the greater the incidence of significant carbon monoxide exposure.

Carboxyhaemoglobin levels in blood donors have been studied for various urban populations in the USA. Included have been studies of blood donors and sources of carbon monoxide in the metropolitan St. Louis, Missouri, population (Kahn et al., 1974); evaluation of smoking and carboxyhaemoglobin in the St. Louis metropolitan population (Wallace et al., 1974); carboxyhaemoglobin analyses of 16,649 blood samples provided by the Red Cross Missouri–Illinois blood donor programme (Davis & Gantner, 1974); a survey of blood donors for percent carboxyhaemoglobin in Chicago, Illinois, Milwaukee, Wisconsin, New York, New York, and Los Angeles, California (Stewart et al., 1976); a national survey for carboxyhaemoglobin in American blood donors from urban, suburban and rural communities across the USA (Stewart et al., 1974); and the trend in percent carboxyhaemoglobin associated with vehicular traffic in Chicago blood donors (Stewart et al., 1976). These extensive studies of volunteer blood donor populations show three main sources of exposure to carbon monoxide in urban environments: smoking, general activities (usually associated with internal combustion engines) and occupational exposures. For comparisons of sources, the populations are divided into two main groups — smokers and non-smokers. The main groups are often divided further into subgroups consisting of industrial workers, drivers, pedestrians and others, for example. Among the two main groups, smokers show an average of 4% carboxyhaemoglobin, with a usual range of 3–8%; non-smokers average about 1% carboxyhaemoglobin (Radford & Drizd, 1982). Smoking behaviour generally occurs as an intermittent diurnal pattern, but carboxyhaemoglobin levels can rise to a maximum of about 15% in some individuals who chain-smoke. Similar results were obtained in a more recent study in Bahrain (Madany, 1992) and in a study in Beijing, People’s Republic of China (Song et al., 1984).

Aside from tobacco smoke, the most significant sources of potential exposure to carbon monoxide in the population are community air pollution, occupational exposures and household exposures (Goldsmith, 1970). Community air pollution comes mainly from...
automobile exhaust and has a typical intermittent diurnal pattern. Occupational exposures occur for up to 8 h per day, 5 days per week, producing carboxyhaemoglobin levels generally less than 10%.

More recent studies characterizing carboxyhaemoglobin levels in the population have appeared in the literature. Turner et al. (1986) used an IL 182 CO-Oximeter to determine percent carboxyhaemoglobin in venous blood of a study group consisting of both smoking and non-smoking hospital staff, inpatients and outpatients. Blood samples were collected for 3487 subjects (1255 non-smokers) during morning hours over a 5-year period. A detailed smoking history was obtained at the time of blood collection. Using 1.7% carboxyhaemoglobin as a normal cut-off value, the distribution for the population studied showed above-normal results for 94.7% of cigarette smokers, 10.3% of primary cigar smokers, 97.4% of those exposed to environmental smoke from cigars and 94.7% of those exposed to environmental smoke from pipes.

Zwart & van Kampen (1985) tested a blood supply using a routine spectrophotometric method for total haemoglobin and for carboxyhaemoglobin in 3022 samples of blood for transfusion in hospital patients in the Netherlands. For surgery patients over a 1-year period, the distribution of percent carboxyhaemoglobin in samples collected as part of the surgical protocol showed 65% below 1.5% carboxyhaemoglobin, 26.5% between 1.5% and 5% carboxyhaemoglobin, 6.7% between 5% and 10% carboxyhaemoglobin and 0.3% in excess of 10% carboxyhaemoglobin. This distribution of percent carboxyhaemoglobin was homogeneous across the entire blood supply, resulting in 1 in 12 patients having blood transfusions at 75% available haemoglobin capacity.

Radford & Drizd (1982) analysed blood carboxyhaemoglobin in approximately 8400 samples obtained from respondents in the 65 geographic areas of the second US National Health and Nutrition Examination Survey during the period 1976–1980. When the frequency distributions of blood carboxyhaemoglobin levels are plotted on a logarithmic probability scale to facilitate comparison of the results for different age groups and smoking habits, it is evident that adult smokers in the USA have carboxyhaemoglobin levels considerably higher than those of non-smokers, with 79% of the smokers’ blood samples above 2% carboxyhaemoglobin and 27% of the
observations above 5% carboxyhaemoglobin. The nationwide distributions of persons aged 12–74 who have never smoked and who are ex-smokers were similar, with 5.8% of the ex-smokers and 6.4% of the never-smokers above 2% carboxyhaemoglobin. It is evident that a significant proportion of the non-smoking US population had blood levels above 2% carboxyhaemoglobin. For these two non-smoking groups, blood levels above 5% were found in 0.7% of the never-smokers and 1.5% of the ex-smokers. It is possible that these high blood levels could be due, in part, to misclassification of some smokers as either ex- or non-smokers. Children aged 2–11 had lower carboxyhaemoglobin levels than the other groups, with only 2.3% of the children’s samples above 2% carboxyhaemoglobin and 0.2% above 5% carboxyhaemoglobin.

Wallace & Ziegenfus (1985) utilized available data from the second National Health and Nutrition Examination Survey to analyse the relationship between measured carboxyhaemoglobin levels and the associated 8-h carbon monoxide concentrations at nearby fixed monitors. Carboxyhaemoglobin data were available for a total of 1658 non-smokers in 20 cities. The authors concluded that fixed outdoor carbon monoxide monitors alone are, in general, not providing useful estimates of carbon monoxide exposure of urban residents.

5.4.2 Breath measurements in populations

In a study by Wallace (1983) in which breath measurements of carbon monoxide were used to detect an indoor air problem, 65 workers in an office had been complaining for some months of late-afternoon sleepiness and other symptoms, which they attributed to the new carpet. About 40 of the workers had their breath tested for carbon monoxide on a Friday afternoon and again on a Monday morning. The average breath carbon monoxide levels decreased from 26 mg/m$^3$ (23 ppm) on Friday to 8 mg/m$^3$ (7 ppm) on Monday morning, indicating a work-related condition. Non-working fans in the parking garage and broken fire doors were identified as the cause of the problem.

Wald et al. (1981) obtained measurements of percent carboxyhaemoglobin for 11 749 men, aged 35–64, who attended a medical centre in London, United Kingdom, for comprehensive health screening examinations between 11:00 a.m. and 5:00 p.m. The time of smoking for each cigarette, cigar or pipe smoked since waking was
recorded at the time of collection of a venous blood sample. Percent carboxyhaemoglobin was determined using an IL 181 CO-Oximeter. Using 2% carboxyhaemoglobin as a normal cut-off value, 81% of cigarette smokers, 35% of cigar and pipe smokers and 1% of non-smokers were found to be above normal. An investigation of carboxyhaemoglobin and alveolar carbon monoxide was conducted on a subgroup of 187 men (162 smokers and 25 non-smokers). Three samples of alveolar air were collected at 2-min intervals within 5 min of collecting venous blood for carboxyhaemoglobin estimation. Alveolar air was collected by having the subject hold his breath for 20 s and then exhale through a 1-m glass tube with an internal diameter of 17 mm and fitted with a 3-litre anaesthetic bag at the distal end. Air at the proximal end of the tube was considered to be alveolar air, and a sample was removed by a small side tube located 5 mm from the mouthpiece. The carbon monoxide content was measured using an Ecolyzer. The instrumental measurement is based on detection of the oxidation of carbon monoxide to carbon dioxide by a catalytically active electrode in an aqueous electrolyte. The mean of the last two readings to the nearest 0.29 mg/m³ (0.25 ppm) was recorded as the alveolar carbon monoxide concentration. Subjects reporting recent alcohol consumption were excluded, because ethanol in the breath affects the response of the Ecolyzer. A linear regression equation of percent carboxyhaemoglobin on alveolar carbon monoxide level had a correlation coefficient of 0.97, indicating that a carboxyhaemoglobin level could be estimated reliably from an alveolar carbon monoxide level.

Honigman et al. (1982) determined alveolar carbon monoxide concentrations by end-expired breath analysis for athletes (joggers). The group included 36 non-smoking males and 7 non-smoking females, all conditioned joggers, covering at least 34 km per week for the previous 6 months in the Denver, Colorado, area. The participants exercised for a 40-min period each day over one of three defined courses in the Denver urban environment (elevation 1610 m). Samples of expired air were collected and analysed before start of exercise, after 20 min and again at the end of the 40-min exercise period. Heart rate measurements at 20 min and 40 min were 84 and 82% of mean age-predicted maxima, respectively, indicating exercise in the aerobic range. Relative changes in carbon monoxide concentrations in expired air were plotted and compared with carbon monoxide concentrations in ambient air measured at the time of
collecting breath samples. Air and breath samples were analysed using an MSA Model 70. Relative changes in expired end-air carbon monoxide based on the concentration of carbon monoxide in breath before the start of exercise were plotted in terms of the ambient air concentrations measured during the exercise period, at both 20 and 40 min of exercise. For ambient concentrations of carbon monoxide below 7 mg/m$^3$ (6 ppm), the aerobic exercise served to decrease the relative amount of expired end-air carbon monoxide compared with the concentration measured before the start of exercise. For ambient concentrations in the range of 7–8 mg/m$^3$ (6–7 ppm), there was no net change in the carbon monoxide concentrations in the expired air. For ambient air concentrations in excess of 8 mg/m$^3$ (7 ppm), the aerobic exercise resulted in relative increases in expired carbon monoxide, with the increases after 40 min being greater than similar increases observed at the 20-min measurements. Sedentary controls at the measurement stations showed no relative changes. Thus, aerobic exercise, as predicted by the physiological models of uptake and elimination, is shown to enhance transport of carbon monoxide, thereby decreasing the time to reach equilibrium conditions.

Verhoeff et al. (1983) surveyed 15 identical residences that used natural gas for cooking and geyser units for water heating. Carbon monoxide concentrations in the flue gases were measured using an Ecolyzer (2000 series). The flue gases were diluted to the dynamic range of the instrument for carbon monoxide (determined by Draeger tube analyses for carbon dioxide dilution to 2.0–2.5%). Breath samples were collected from 29 inhabitants by having each participant hold a deep breath for 20 s and exhale completely through a glass sampling tube (225-ml volume). The sampling tube was stoppered and taken to a laboratory for analysis of carbon monoxide content using a gas–liquid chromatograph (Hewlett-Packard 5880A). The overall coefficient of variation for sampling and analysis was 7%, based on results of previous measurements. No significant differences were observed for non-smokers as a result of their cooking or dishwashing activities using the natural gas fixtures. There was a slight increase in carbon monoxide in expired air for smokers, but this may be due to the possibility of increased smoking during the dinner hour.

Wallace et al. (1984) reported data on measurements of expired end-air carbon monoxide and comparisons with predicted values based on personal carbon monoxide measurements for populations in
Denver, Colorado, and Washington, DC. Correlations between breath carbon monoxide and preceding 8-h average carbon monoxide exposures were high (0.6–0.7) in both cities. Correlation coefficients were calculated for 1-h to 10-h average personal carbon monoxide exposures in 1-h increments; the highest correlations occurred at 7–9 h. However, breath carbon monoxide levels showed no relationship with ambient carbon monoxide measurements at the nearest fixed-station monitor.

A major large-scale study employing breath measurements of carbon monoxide was carried out by the US EPA in Washington, DC, and Denver, Colorado, in the winter of 1982–83 (Hartwell et al., 1984; Johnson, 1984; Wallace et al., 1984, 1988; Akland et al., 1985). In Washington, DC, 870 breath samples were collected from 812 participants; 895 breath samples were collected from 454 Denver participants (two breath samples on 2 consecutive days in Denver). All participants also carried personal monitors to measure their exposures over a 24-h period in Washington, DC, or a 48-h period in Denver. The subjects in each city formed a probability sample representing 1.2 million adult non-smokers in Washington, DC, and 500 000 adult non-smokers in Denver.

The distributions of breath levels in the two cities appeared to be roughly lognormal, with geometric means of 6.0 mg carbon monoxide/m$^3$ (5.2 ppm) for Denver and 5.0 mg carbon monoxide/m$^3$ (4.4 ppm) for Washington, DC. Geometric standard deviations were about 1.8 mg/m$^3$ (1.6 ppm) for each city. Arithmetic means were 8.1 mg/m$^3$ (7.1 ppm) for Denver and 6.0 mg/m$^3$ (5.2 ppm) for Washington, DC.

Of greater regulatory significance is the number of people whose carboxyhaemoglobin levels exceeded the value of 2.1%, because the US EPA has determined that the current 10 mg/m$^3$ (9 ppm), 8-h average standard would keep more than 99.9% of the most sensitive non-smoking adult population below this level of protection (Federal Register, 1985). An alveolar carbon monoxide concentration of about 11 mg/m$^3$ (10 ppm) would correspond to a carboxyhaemoglobin level of 2%. The percentage of people with measured breath values exceeding this level was about 6% in Washington, DC. This percentage was increased to 10% when the correction for the effect of room air was applied. Of course, because the breath samples were taken on
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days and at times when carbon monoxide levels were not necessarily at their highest level during the year, these percentages are lower limits of the estimated number of people who may have incurred carboxyhaemoglobin levels above 2%. Yet the two central stations in Washington, DC, recorded a total of one exceedance of the 10 mg/m³ (9 ppm) standard during the winter of 1982–83. Models based on fixed-station readings would have predicted that an exceedingly tiny proportion of the Washington, DC, population received exposures exceeding the standard. Therefore, the results from the breath measurements indicated that a much larger portion of both Denver and Washington, DC, residents were exceeding 2% carboxyhaemoglobin than was predicted by models based on fixed-station measurements.

It should also be noted that the number of people with measured maximum 8-h exposures exceeding the EPA outdoor standard of 10 mg/m³ (9 ppm) was only about 3.5% of the Washington, DC, subjects. This value appears to disagree with the value of 10% obtained from the corrected breath samples. However, the personal monitors used in the study were shown to experience several different problems, including a loss of response associated with battery discharge towards the end of the 24-h monitoring period, which caused them to read low just at the time the breath samples were being collected. Therefore, Wallace et al. (1988) concluded that the breath measurements were correct and the personal air measurements were biased low. The importance of including breath measurements in future exposure and epidemiology studies is indicated by this study.

Hwang et al. (1984) described the use of expired air analysis for carbon monoxide in an emergency clinical setting to diagnose the presence and extent of carbon monoxide intoxication. The subjects were 47 Korean patients brought in for emergency treatment who showed various levels of consciousness: alertness (11), drowsiness (21), stupor (7), semicoma (5), coma (1) and unknown (2). The study group included 16 males, aged 16–57, and 31 females, aged 11–62. Exposure durations ranged from 2 to 10 h, with all exposures occurring in the evening and nighttime hours. The source of carbon monoxide was mainly charcoal fires used for cooking and heating. In order to estimate carbon monoxide concentrations in expired air, a detector tube (Gastec 1La containing potassium palladosulfite as both a reactant and colour-change indicator for the presence of carbon monoxide on silica gel) was fitted to a Gastec manual sampling pump.
One stroke of the sampling plunger represents 100 ml of air. A 100-ml sample of expired air was collected by inserting a detector tube at a nostril and slowly pulling back the plunger for one full stroke for expired air. A 10-ml sample of venous blood was also collected at this time for determining percent carboxyhaemoglobin using a CO-Oximeter. The subjects showed signs of acute intoxication, and significant relationships were found between carbon monoxide levels in expired air and percent carboxyhaemoglobin.

Cox & Whichelow (1985) analysed end-exhaled air (collected over approximately the last half of the exhalation cycle) for carbon monoxide concentrations for a random population of 168 adults — 69 smokers and 99 non-smokers. The results were used to evaluate the influence of home heating systems on exposures to and absorption of carbon monoxide. Ambient indoor concentrations of carbon monoxide were measured in the homes of study subjects. The subjects included 86 men and 82 women, ranging in age from 18 to 74. Interviews were usually conducted in the living room of the subject’s home. The type of heating system in use was noted, and the indoor air concentration of carbon monoxide was measured using an Ecolyzer. After the ambient indoor carbon monoxide level was determined, a breath sample was collected from the subject. The subject was asked to hold a deep breath for 20 s and then to exhale completely into a trilaminate plastic bag. The bag was fitted to the port of the Ecolyzer, and the carbon monoxide content of the exhaled air was measured. For smokers, the time since smoking their last cigarette and the number of cigarettes per day were noted. For non-smokers, there was a strong correlation between carbon monoxide levels in ambient air and carbon monoxide levels in expired air. With smokers, the correlation was strongest with the number of cigarettes smoked per day. The data also supported the supposition that smokers are a further source of ambient carbon monoxide in the indoor environment.

Lambert et al. (1988) compared carbon monoxide levels in breath with carboxyhaemoglobin levels in blood in 28 subjects (including 2 smokers). Breath carbon monoxide was collected using the standard technique developed by Jones et al. (1958): maximal inspiration was followed by a 20-s breath-hold, and the first portion of the expired breath was discarded. Excellent precision (± 0.23 mg/m$^3$ [± 0.2 ppm]) was obtained in 35 duplicate samples. Blood samples were collected within 15 min of the breath samples using a gas-tight plastic syringe.
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rinsed with sodium heparin. Carboxyhaemoglobin was measured using an IL 282 CO-Oximeter. Some samples were also measured using a gas chromatograph.

By using least squares regression, the null hypothesis of no difference in the slope and intercept estimates for non-smokers and smokers was not rejected (i.e., there was no association between blood carboxyhaemoglobin and breath carbon monoxide in either non-smokers or smokers).

5.4.3 Subject age

The relationship between age and carboxyhaemoglobin level is not well established. Kahn et al. (1974) reported that non-smoking subjects under the age of 19 years had a significantly lower percent carboxyhaemoglobin than older subjects, but there was no difference in carboxyhaemoglobin between the ages of 20 and 59 years. Kahn et al. (1974) also reported that there was a slight decrease in the carboxyhaemoglobin levels in non-smoking subjects over the age of 60 years. Radford & Drizd (1982) reported that younger subjects, 3–11 years old, had lower levels of carboxyhaemoglobin than did the older age group of 12–74 years. Goldsmith (1970) reported that expired carbon monoxide levels were unchanged with age in non-smokers; however, there was a steady decline in the expired carbon monoxide levels with age in smokers. The decrease in expired carbon monoxide is disproportionately large for the decrease in carboxyhaemoglobin levels measured by Kahn et al. (1974) in older subjects. Therefore, by comparison of the data from these two studies, it would appear that older subjects have higher levels of carboxyhaemoglobin than predicted from the expired carbon monoxide levels. It is not known how much of this effect is due to aging of the pulmonary system, resulting in a condition similar to that of subjects with obstructive pulmonary disease (see below).

5.4.4 Pulmonary disease

A major potential influence on the relationship between blood and alveolar partial pressures of carbon monoxide is the presence of significant lung disease. Hackney et al. (1962) demonstrated that the slow increase in exhaled carbon monoxide concentration in a rebreathing system peaked after 1.5 min in healthy subjects but required 4 min in a subject with lung disease. These findings have
been substantiated by Guyatt et al. (1988), who reported that patients with pulmonary disease did not have the same relationship between percent carboxyhaemoglobin and breath-hold carbon monoxide concentrations. The group with pulmonary disease had a forced expiratory volume in 1 s (FEV₁)/forced vital capacity (FVC) percentage of <71.5%, whereas the healthy subjects had an FEV₁/FVC percentage of >86%. The linear regression for the healthy group was \( \text{COHb} = 0.629 + 0.158(\text{ppm CO}) \); for the pulmonary disease group, the linear regression was \( \text{COHb} = 0.369 + 0.185(\text{ppm CO}) \). This means that at low carbon monoxide levels, individuals with obstructive pulmonary disease would have a lower “alveolar” carbon monoxide level for any given percent carboxyhaemoglobin level than would the healthy subjects.

### 5.4.5 Effects of smoking

Studies evaluating the effect of cigarette smoking on end-expired carbon monoxide have found a phasic response that depends on smoking behaviour (Henningfield et al., 1980; Woodman et al., 1987). There is an initial rapid increase in the carbon monoxide concentration of expired air as a result of smoking. This is followed by a rapid (5-min) decrease after cessation of smoking and a slow decrease over the 5- to 60-min period after smoking. A comparison of the results from one study (Tsukamoto & Matsuda, 1985) showed that the carbon monoxide concentration in expired air increases by approximately 6 mg/m³ (5 ppm) after smoking one cigarette. This corresponds to an increase of 0.67% carboxyhaemoglobin based on blood–breath relationships developed by the authors. Use of cigarettes with different tar and nicotine yields or the use of filter-tip cigarettes showed no apparent effect on end-expired carbon monoxide concentrations (Castelli et al., 1982).

The relationship between breath-hold carbon monoxide and blood carbon monoxide is apparently altered as a result of smoking, making the detection of small changes difficult. Guyatt et al. (1988) showed that smoking one cigarette results in a variable response in the relationship between breath-hold alveolar carbon monoxide fraction \( [F_{A,CO(Bh)}] \) and carboxyhaemoglobin levels. The range of \( F_{A,CO(Bh)} \) values for an increase of 1% carboxyhaemoglobin was from \( ! 0 \) to +6 mg/m³ (\( ! 5 \) to +5 ppm). The correlation between the change in \( F_{A,CO(Bh)} \) and the change in carboxyhaemoglobin in 500 subjects was only 0.705. This \( r \) value indicates that only 50% of the change in \( F_{A,CO(Bh)} \) was due to changes in carboxyhaemoglobin. It is not
known how much of this residual error is due to subject compliance or to error in the method. Therefore, the results obtained with breath-holding in smoking subjects should be viewed with caution unless large differences in $F_{CO(Bh)}$ are reported (i.e., considerable cigarette consumption is being evaluated).

### 5.5 Megacities and other major urban areas

Throughout the world, there are large urban areas that have serious air pollution problems and encompass large land areas and over 10 million people (total population of the 20 megacities in 1990 was estimated to be 275 million). The cities that have been designated as megacities include 2 in North America (Los Angeles, California, USA; New York, New York, USA), 4 in Central and South America (Buenos Aires, Argentina; Mexico City, Mexico; Rio de Janeiro, Brazil; São Paulo, Brazil), 1 in Africa (Cairo, Egypt), 11 in Asia (Bangkok, Thailand; Beijing, People’s Republic of China; Bombay, India; Calcutta, India; Delhi, India; Jakarta, Indonesia; Karachi, Pakistan; Manila, Philippines; Seoul, South Korea; Shanghai, People’s Republic of China; Tokyo, Japan) and 2 in Europe (London, United Kingdom; Moscow, Russia). However, many other cities are heading for megacity status.

Of the 20 megacities studied (WHO/UNEP, 1992; Mage et al., 1996), monitoring capabilities for carbon monoxide have been designated as none or unknown in 9, rudimentary in 1, adequate in 4 and good in 6 (see Table 7). The air quality for carbon monoxide has been designated as no data available or insufficient data for assessment in six; serious problems, WHO guidelines exceeded by more than a factor of 2 in one; moderate to heavy pollution, WHO guidelines exceeded by up to a factor of 2 (short-term guidelines exceeded on a regular basis at certain locations) in seven; and low pollution, WHO guidelines are normally met (short-term guidelines may be exceeded occasionally) in six (see Table 7).

The problem of air pollution in Mexico City is confounded by geography. The metropolitan area of Mexico City is located at a mean altitude of 2240 m and is situated in the Mexican Basin. The reduced oxygen in the air at high altitude causes carbon monoxide emissions to increase because of incomplete combustion, and it exacerbates the health effects attributed to carbon monoxide, especially among highly
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Table 7. Overview of carbon monoxide air quality and monitoring capabilities in 20 megacities

<table>
<thead>
<tr>
<th>Megacity</th>
<th>Air quality for carbon monoxide</th>
<th>Status of monitoring capabilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bangkok, Thailand</td>
<td>a</td>
<td>B</td>
</tr>
<tr>
<td>Beijing, People’s Republic of China</td>
<td>d</td>
<td>B</td>
</tr>
<tr>
<td>Bombay, India</td>
<td>a</td>
<td>D</td>
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<tr>
<td>Buenos Aires, Argentina</td>
<td>d</td>
<td>D</td>
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<tr>
<td>Cairo, Egypt</td>
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<td>D</td>
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<td>Calcutta, India</td>
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<tr>
<td>Delhi, India</td>
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<td>D</td>
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<tr>
<td>Jakarta, Indonesia</td>
<td>b</td>
<td>D</td>
</tr>
<tr>
<td>Karachi, Pakistan</td>
<td>d</td>
<td>D</td>
</tr>
<tr>
<td>London, United Kingdom</td>
<td>b</td>
<td>B</td>
</tr>
<tr>
<td>Los Angeles, USA</td>
<td>b</td>
<td>A</td>
</tr>
<tr>
<td>Manila, Philippines</td>
<td>d</td>
<td>D</td>
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<tr>
<td>Mexico City, Mexico</td>
<td>c</td>
<td>A</td>
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<tr>
<td>Moscow, Russia</td>
<td>b</td>
<td>C</td>
</tr>
<tr>
<td>New York, USA</td>
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<td>A</td>
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<tr>
<td>Rio de Janeiro, Brazil</td>
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<td>B</td>
</tr>
<tr>
<td>São Paulo, Brazil</td>
<td>b</td>
<td>A</td>
</tr>
<tr>
<td>Seoul, South Korea</td>
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<td>A</td>
</tr>
<tr>
<td>Shanghai, People’s Republic of China</td>
<td>d</td>
<td>D</td>
</tr>
<tr>
<td>Tokyo, Japan</td>
<td>a</td>
<td>A</td>
</tr>
</tbody>
</table>

*a* Adapted from WHO/UNEP (1992); Mage et al. (1996).

*Adapted from WHO/UNEP (1992); Mage et al. (1996).*

- **a** = Low pollution, WHO guidelines normally met (short-term guidelines may be exceeded occasionally).
- **b** = Moderate to heavy pollution, WHO guidelines exceeded by up to a factor of 2 (short-term guidelines exceeded on a regular basis at certain locations).
- **c** = Serious problem, WHO guidelines exceeded by more than a factor of 2.
- **d** = No data available or insufficient data for assessment.

*Good.*

*Good.*

*Adequate.*

*Rudimentary.*

*None or not known.*
susceptible population groups, including children and pregnant women.

Data for air quality trends in about 40 countries were collected in the WHO/United Nations Environment Programme (UNEP) Global Environmental Monitoring System (GEMS/Air) (UNEP/WHO, 1993). The GEMS/Air programme was terminated in 1995. WHO has set up a successive programme, the Air Management Information System (WHO, 1997a). Summary air quality data for carbon monoxide are currently available for many countries, such as Austria, Germany, Greece, Japan, New Zealand and Switzerland. For example, between 1986 and 1995, the annual mean carbon monoxide concentrations ranged from 5.1 to 8.4 mg/m$^3$ (4.5 to 7.3 ppm) in Greece, from 0.8 to 2.7 mg/m$^3$ (0.7 to 2.4 ppm) in Japan and from 0.9 to 1.9 mg/m$^3$ (0.8 to 1.7 ppm) in New Zealand. In Australia, the annual mean carbon monoxide concentrations from 1988 to 1995 ranged from 0.66 to 1.36 mg/m$^3$ (0.58 to 1.19 ppm). Air quality trends for carbon monoxide over the same period are shown in Fig. 3 for Athens, Greece, Chongqing, People’s Republic of China, Frankfurt, Germany, Johannesburg, South Africa, London, United Kingdom, and Los Angeles, USA.

In a recent report (Eerens et al., 1995), carbon monoxide data from 105 cities in 35 European states are given. They include annual average 8-h maximum concentrations and number of days exceeding WHO Air Quality Guidelines and twice the WHO Air Quality Guidelines.

### 5.6 Indoor concentrations and exposures

Indoor concentrations of carbon monoxide are a function of outdoor concentrations, indoor sources (source type, source condition, source use, etc.), infiltration/ventilation and air mixing between and within rooms. In residences without sources, average carbon monoxide concentrations are approximately equal to average outdoor concentrations at the corresponding elevation, generally decreasing with height above the ground. Proximity to outdoor sources (i.e., structures near heavily travelled roadways or with attached garages or parking garages) can have a major impact on indoor carbon monoxide concentrations.
Fig. 3. Trends in carbon monoxide air quality between 1986 and 1995 in Johannesburg (South Africa), Frankfurt (Germany), London (United Kingdom), Athens (Greece), Los Angeles (USA) and Chongqing (China) (from WHO, 1997a).
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Athens, Greece

![Graph showing carbon monoxide concentration in Athens, Greece from 1986 to 1995. The graph includes data for industrial, commercial, and residential concentrations.](graph)

Los Angeles, USA

![Graph showing 95-percentile concentration in Los Angeles, USA from 1986 to 1995.](graph)

Chongqing, China

![Graph showing concentration in Chongqing, China from 1983 to 1994.](graph)

Fig. 3. (contd).
The development of small lightweight and portable electrochemical carbon monoxide monitors over the past decade has permitted the measurement of personal carbon monoxide exposures and carbon monoxide concentrations in a number of indoor environments. The available data on indoor carbon monoxide concentrations have been obtained from total personal exposure studies or studies in which various indoor environments have been targeted for measurements.

The extensive total personal carbon monoxide exposure studies conducted by the US EPA in Washington, DC, and Denver, Colorado, have shown that the highest carbon monoxide concentrations occur in indoor microenvironments associated with transportation sources (parking garages, cars, buses, etc.). Concentrations in these environments were found to frequently exceed 10 mg/m$^3$ (9 ppm). Studies targeted towards specific indoor microenvironments have also identified the in-vehicle commuting microenvironment as an environment in which carbon monoxide concentrations frequently exceed 10 mg/m$^3$ (9 ppm) and occasionally exceed 40 mg/m$^3$ (35 ppm). Special environments or occurrences (indoor ice skating rinks, offices where emissions from parking garages migrate indoors, etc.) have been reported where indoor carbon monoxide levels can exceed the recommended air quality guidelines.

A majority of the targeted field studies (see section 5.6.2) monitored indoor carbon monoxide levels as a function of the presence or absence of combustion sources (gas ranges, unvented gas and kerosene space heaters, wood-burning stoves and fireplaces and tobacco combustion). The results of these studies indicate that the presence and use of an unvented combustion source result in indoor carbon monoxide levels above those found outdoors. The associated increase in carbon monoxide concentrations can vary considerably as a function of the source, source use, condition of the source and averaging time of the measurement. Intermittent sources such as gas cooking ranges can result in high peak carbon monoxide concentrations (in excess of 10 mg/m$^3$ [9 ppm]), whereas long-term average increases in concentrations (i.e., 24-h) associated with gas ranges are considerably lower (on the order of 1.1 mg/m$^3$ [1 ppm]). The contribution of tobacco combustion to indoor carbon monoxide levels is variable. Under conditions of high smoking and low ventilation, the contribution can be on the order of a few milligrams per cubic metre (parts per million). One study suggested that the contribution to
residential carbon monoxide concentrations of tobacco combustion is on the order of 1.1 mg/m³ (1 ppm), whereas another study showed no significant increase in residential carbon monoxide levels.

Unvented or poorly vented combustion sources that are used for substantial periods of time (e.g., unvented gas and kerosene space heaters) appear to be the major contributors to residential carbon monoxide concentrations. One extensive study of unvented gas space heaters indicated that 12% of the homes had 15-h average carbon monoxide concentrations greater than 9 mg/m³ (8 ppm), with the highest concentration at 41.9 mg/m³ (36.6 ppm). Only very limited data are available on the contribution of kerosene heaters to the average carbon monoxide concentrations in residences, and these data indicate a much lower contribution than that of gas heaters. Peak carbon monoxide concentrations associated with both unvented gas and kerosene space heaters can exceed the current ambient 1- and 8-h standards (40 and 10 mg/m³ [35 and 9 ppm], respectively) in residences, and, because of the nature of the source (continuous), those peaks tend to be sustained for several hours.

Very limited data on carbon monoxide levels in residences with wood-burning stoves or fireplaces are available. Non-airtight stoves can contribute substantially to residential carbon monoxide concentrations, whereas airtight stoves can result in small increases. The available data indicate that fireplaces do not contribute measurably to average indoor concentrations. No information is available for samples of residences with leaky flues. In addition, there is no information available on short-term indoor carbon monoxide levels associated with these sources, nor are there studies that examine the impact of attached garages on residential carbon monoxide concentrations.

The available data on short-term (1-h) and long-term (8-h) indoor carbon monoxide concentrations as a function of microenvironments and sources in those microenvironments are not adequate to assess exposures in those environments. In addition, little is known about the spatial variability of carbon monoxide indoors. These indoor microenvironments represent the most important carbon monoxide exposures for individuals and as such need to be better characterized.

Concentrations of carbon monoxide in an enclosed environment are affected by a number of factors in addition to the source factors.
These factors include outdoor concentrations, proximity to outdoor sources (i.e., parking garages or traffic), volume of the space and mixing within and between indoor spaces.

Carbon monoxide measurements in enclosed spaces have been made either in support of total personal exposure studies or in targeted indoor studies. In the personal exposure studies, individuals wear the monitors in the course of their daily activities, taking them through a number of different microenvironments. In targeted studies, carbon monoxide measurements are taken in indoor spaces independent of the activities of occupants of those spaces.

5.6.1 Indoor concentrations recorded in personal exposure studies

Three studies have reported carbon monoxide concentrations in various microenvironments as part of an effort to measure total human exposure to carbon monoxide and to assess the accuracy of exposure estimates calculated from fixed-site monitoring data. In each study, subjects wore personal carbon monoxide exposure monitors for one or more 24-h periods. Carbon monoxide concentrations were recorded on data loggers at varying time intervals as a function of time spent in various microenvironments. Participants kept an activity diary in which they were asked to record time, activity (e.g., cooking), location (microenvironment type), presence and use of sources (e.g., smokers or gas stoves) and other pertinent information. Carbon monoxide concentrations by microenvironment were extracted from the measured concentrations by use of the activity diaries.

Two of the studies, conducted in Denver, Colorado, and Washington, DC, by the US EPA (Hartwell et al., 1984; Johnson, 1984; Whitmore et al., 1984; Akland et al., 1985), measured the frequency distribution of carbon monoxide exposure in a representative sample of the urban population. The study populations were selected using a multistage sampling strategy. The third study, also conducted in Washington, DC (Nagda & Koontz, 1985), utilized a convenience sample.

The first-mentioned Washington, DC, study obtained a total of 814 person-day samples for 1161 participants, whereas the Denver study obtained 899 person-day samples for 485 participants. The Denver study obtained consecutive 24-h samples for each participant, whereas the Washington, DC, study obtained one 24-h sample for
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Each participant. Both studies were conducted during the winter of 1982–83.

A comparison of carbon monoxide concentrations measured in the Washington, DC, and Denver studies is shown in Table 8 (from Akland et al., 1985). Concentrations measured in all microenvironments for the Denver study were higher than those for the Washington, DC, study. This is consistent with the finding that daily maximum 1-h and 8-h carbon monoxide concentrations at outdoor fixed monitoring sites were about a factor of 2 higher in the Denver area than in the Washington, DC, area during the course of the studies (Akland et al., 1985). The highest concentrations in both studies were associated with indoor parking garages and commuting, whereas the lowest levels were measured in indoor environments without sources of carbon monoxide. Concentrations associated with commuting are no doubt higher owing to the proximity to and density of outside carbon monoxide sources (cars, buses and trucks), particularly during commuting hours when traffic is heaviest. Indoor levels, especially residential levels in the absence of indoor sources, are lower primarily because of the time of day of sampling (non-commuting hours with lower outdoor levels). A more detailed breakdown of carbon monoxide concentrations by microenvironments for the Denver study is shown in Table 9 (Johnson, 1984). Microenvironments associated with motor vehicles result in the highest concentrations, with concentrations reaching or exceeding the NAAQS 10 mg/m$^3$ (9 ppm) reference level.

No statistical difference ($P > 0.05$) in carbon monoxide concentrations was found between residences with and without gas ranges in the Washington, DC, study. The results of a similar analysis on the Denver data, according to the presence or absence of selected indoor sources, are shown in Table 10 (Johnson, 1984); in contrast to the Washington, DC, study, the presence of an operating gas stove in the Denver study resulted in a statistically significant increase of 2.97 mg/m$^3$ (2.59 ppm). Attached garages, use of gas ranges and presence of smokers were all shown to result in higher indoor carbon monoxide concentrations. Concentrations were well below the NAAQS 10 mg/m$^3$ (9 ppm) reference level but were substantially above concentrations in residences without the sources.

In the second Washington, DC, study (Nagda & Koontz, 1985), 197 person-days of samples were collected from 58 subjects,
<table>
<thead>
<tr>
<th>Microenvironment</th>
<th>Denver, Colorado</th>
<th></th>
<th>Median time (min)</th>
<th>Washington, DC</th>
<th>CO concentration (mean ± SE)$^b$</th>
<th>Median time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO concentration (mean ± SE)$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indoors, parking garage</td>
<td>31</td>
<td>21.5 ± 5.68 mg/m$^3$</td>
<td>18.8 ± 4.96 ppm</td>
<td>14</td>
<td>59</td>
<td>11.9 ± 5.07 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21.5 ± 5.68 ppm</td>
<td></td>
<td></td>
<td>18.8 ± 4.96 mg/m$^3$</td>
<td></td>
</tr>
<tr>
<td>Indoors, walking</td>
<td>171</td>
<td>4.8 ± 0.52 mg/m$^3$</td>
<td>4.2 ± 0.45 ppm</td>
<td>28</td>
<td>226</td>
<td>2.7 ± 0.33 ppm</td>
</tr>
<tr>
<td>Indoors, shopping mall</td>
<td>243</td>
<td>3.4 ± 0.25 mg/m$^3$</td>
<td>3.0 ± 0.22 ppm</td>
<td>50</td>
<td>225</td>
<td>2.9 ± 0.56 ppm</td>
</tr>
<tr>
<td>Indoors, residence</td>
<td>776</td>
<td>1.9 ± 0.11 mg/m$^3$</td>
<td>1.7 ± 0.10 ppm</td>
<td>975</td>
<td>705</td>
<td>1.4 ± 0.11 ppm</td>
</tr>
<tr>
<td>Indoors, total</td>
<td>776</td>
<td>2.4 ± 0.10 mg/m$^3$</td>
<td>2.1 ± 0.09 ppm</td>
<td>1243</td>
<td>705</td>
<td>1.6 ± 0.09 ppm</td>
</tr>
</tbody>
</table>

$^a$ From Akland et al. (1985); $^b$ n = number of person-days with non-zero durations; SE = standard error.
Table 9. Indoor microenvironments in Denver, Colorado, listed in descending order of weighted mean carbon monoxide concentration

<table>
<thead>
<tr>
<th>Category</th>
<th>Number of observations</th>
<th>CO concentration (mean ± SD)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mg/m(^3)</td>
</tr>
<tr>
<td>Public garage</td>
<td>116</td>
<td>15.41 ± 20.77</td>
</tr>
<tr>
<td>Service station or motor vehicle repair facility</td>
<td>125</td>
<td>10.50 ± 10.68</td>
</tr>
<tr>
<td>Other location</td>
<td>427</td>
<td>8.47 ± 20.58</td>
</tr>
<tr>
<td>Other repair shop</td>
<td>55</td>
<td>6.46 ± 8.78</td>
</tr>
<tr>
<td>Shopping mall</td>
<td>58</td>
<td>5.61 ± 7.44</td>
</tr>
<tr>
<td>Residential garage</td>
<td>66</td>
<td>4.98 ± 8.08</td>
</tr>
<tr>
<td>Restaurant</td>
<td>524</td>
<td>4.25 ± 4.98</td>
</tr>
<tr>
<td>Office</td>
<td>2287</td>
<td>4.11 ± 4.79</td>
</tr>
<tr>
<td>Auditorium, sports arena, concert hall, etc.</td>
<td>100</td>
<td>3.86 ± 5.45</td>
</tr>
<tr>
<td>Store</td>
<td>734</td>
<td>3.70 ± 6.37</td>
</tr>
<tr>
<td>Health care facility</td>
<td>351</td>
<td>2.54 ± 4.89</td>
</tr>
<tr>
<td>Other public buildings</td>
<td>115</td>
<td>2.46 ± 3.73</td>
</tr>
<tr>
<td>Manufacturing facility</td>
<td>42</td>
<td>2.34 ± 2.92</td>
</tr>
<tr>
<td>Residence</td>
<td>21,543</td>
<td>2.34 ± 4.65</td>
</tr>
<tr>
<td>School</td>
<td>426</td>
<td>1.88 ± 3.16</td>
</tr>
<tr>
<td>Church</td>
<td>179</td>
<td>1.79 ± 3.84</td>
</tr>
</tbody>
</table>

\(^a\) Adapted from Johnson et al. (1984).
\(^b\) SD = standard deviation.

representing three population subgroups: housewives, office workers and construction workers. A comparison of residential carbon monoxide concentrations from that study as a function of combustion sources and whether smoking was reported is shown in Table 11. Use of gas ranges and kerosene space heaters was found to result in higher indoor carbon monoxide concentrations. The statistical significance of the differences was not given. Concentrations were highest in microenvironments associated with commuting.

5.6.2 Targeted microenvironmental studies

As demonstrated from the personal exposure studies discussed above, individuals, in the course of their daily activities, can encounter a wide range of carbon monoxide concentrations as a function of the microenvironments in which they spend time. A number of studies have been conducted over the last decade to
Table 10. Weighted means of residential exposure grouped according to the presence or absence of selected indoor carbon monoxide sources in Denver, Colorado

<table>
<thead>
<tr>
<th>CO source</th>
<th>CO concentration (mean ± SD)</th>
<th>Difference in means</th>
<th>Significance level of t-test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Source present</td>
<td>Source absent</td>
<td>mg/m³</td>
</tr>
<tr>
<td>Attached garage</td>
<td>2.62 ± 6.11</td>
<td>2.29 ± 5.34</td>
<td>2.15 ± 3.44</td>
</tr>
<tr>
<td>Operating gas stove</td>
<td>5.18 ± 6.98</td>
<td>4.52 ± 6.10</td>
<td>2.21 ± 4.49</td>
</tr>
<tr>
<td>Smokers</td>
<td>3.98 ± 7.53</td>
<td>3.48 ± 6.58</td>
<td>2.16 ± 4.23</td>
</tr>
</tbody>
</table>

* Adapted from Johnson (1984).
* SD = standard deviation.
* Student t-test was performed on logarithms of personal exposure monitor values.
Environmental Levels and Personal Exposures

Table 11. Average Washington, DC, residential carbon monoxide exposures: impact of combustion appliance use and tobacco smoking

<table>
<thead>
<tr>
<th>Appliances</th>
<th>Reported tobacco smoking²</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>Yes</td>
<td>All cases</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mg/m³ ppm</td>
<td>mg/m³ ppm</td>
<td>mg/m³ ppm</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>1.4</td>
<td>1.2 (66)</td>
<td>1.4</td>
<td>1.2 (78)</td>
</tr>
<tr>
<td>Gas stove</td>
<td>2.5</td>
<td>2.2 (15)</td>
<td>1.5</td>
<td>1.3 (1)</td>
</tr>
<tr>
<td>Kerosene space heater</td>
<td>5.8</td>
<td>5.1 (3)</td>
<td>ND</td>
<td>5.8</td>
</tr>
<tr>
<td>Wood burning</td>
<td>0.8</td>
<td>0.7 (2)</td>
<td>ND</td>
<td>0.8</td>
</tr>
<tr>
<td>Multiple appliances</td>
<td>1.1</td>
<td>1 (1)</td>
<td>ND</td>
<td>1.1</td>
</tr>
<tr>
<td>All cases</td>
<td>1.7</td>
<td>1.5 (87)</td>
<td>1.7</td>
<td>1.5 (13)</td>
</tr>
</tbody>
</table>

² Adapted from Nagda & Koontz (1985).

³ Percentage of subjects’ time in their own residences indicated in parentheses for each category of appliance use and tobacco smoking.

⁴ ND = No data available.

investigate concentrations of carbon monoxide in indoor microenvironments. These “targeted” studies have focused on indoor carbon monoxide concentrations as a function of either the microenvironment or sources in specific microenvironments.

5.6.2.1 Indoor microenvironmental concentrations

A number of studies have investigated carbon monoxide levels in various indoor environments, independent of the existence of specific indoor sources. Major foci of these studies are microenvironments associated with commuting. A wide range of carbon monoxide concentrations were recorded in these studies, with the highest concentrations found in the indoor commuting microenvironments. These concentrations are frequently higher than concentrations recorded at fixed-site monitors but lower than concentrations measured immediately outside the vehicles. Concentrations are generally higher in automobiles than in public transportation microenvironments. A number of the studies noted that carbon monoxide concentrations in commuting vehicles can exceed recommended air quality guidelines. Flachsbart et al. (1987) noted that the most important factors influencing carbon monoxide concentrations inside automobiles
included link-to-link variability (a proxy for traffic density, vehicle mix and roadway setting), day-to-day variability (a proxy for variations in meteorological factors and ambient carbon monoxide concentrations) and time of day. This study noted that with increased automobile speed, interior carbon monoxide concentrations decreased, because grams of carbon monoxide emitted per kilometre travelled decrease with increasing vehicle speed, and the turbulence of vehicle wake increases with increasing vehicle speed.

Service stations, car dealerships, parking garages and office spaces that have attached garages can exhibit high concentrations of carbon monoxide as a result of automobile exhaust. In one case (Wallace, 1983), corrective measures reduced office space carbon monoxide concentrations originating from an attached parking garage from 22 mg/m$^3$ (19 ppm) to approximately 5 mg/m$^3$ (4 ppm). In an investigation of seven ice skating rinks in the Boston, Massachusetts, area, one study (Spengler et al., 1978) reported exceptionally high average carbon monoxide concentrations (61.4 mg/m$^3$ [53.6 ppm]), with a high reading of 220 mg/m$^3$ (192 ppm). Ice-cleaning machines and poor ventilation were found to be responsible.

Residential and commercial buildings were generally found to have low concentrations of carbon monoxide, but information is seldom provided on the presence of indoor sources or outdoor levels.

5.6.2.2 Concentrations associated with indoor sources

The major indoor sources of carbon monoxide in residences are gas ranges and unvented kerosene and gas space heaters, with properly operating wood-burning stoves and fireplaces (non-leaky venting system) and tobacco combustion of secondary importance. Properly used gas ranges (ranges used for cooking and not space heating) are used intermittently and thus would contribute to short-term peak carbon monoxide levels indoors but likely would not result in substantial increases in longer-term average concentrations. Unvented kerosene and gas space heaters typically are used for several hours at a time and thus are likely to result in sustained higher levels of carbon monoxide. The improper operation of gas ranges or unvented gas or kerosene space heaters (e.g., low-wick setting for kerosene heaters or yellow-tipping operation of gas ranges) could result in substantial increases in indoor carbon monoxide levels. Carbon monoxide levels indoors associated with tobacco combustion...
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are, based upon source emission data, expected to be low unless there is a very high smoking density and low ventilation. In the absence of a leaky flue or leaky fire box, indoor carbon monoxide levels from fireplaces or stoves should be low, with short peaks associated with charging the fire when some backdraft might occur.

The majority of studies investigating carbon monoxide concentrations in residences, as a function of the presence or absence of a known carbon monoxide source, typically have measured carbon monoxide concentrations associated with the source’s use over short periods (on the order of a few minutes to a few hours). Only two studies (Koontz & Nagda, 1987; Research Triangle Institute, 1990) have reported long-term average carbon monoxide concentrations (over several hours) as a function of the presence of a carbon monoxide source for large residential sample sizes, whereas one study (McCarthy et al., 1987) reported longer-term average indoor carbon monoxide concentrations for a small sample.

1) Average indoor-source-related concentrations

As part of a study to determine the impact of combustion sources on indoor air quality, a sample of 382 homes in New York State, USA (172 in Onondaga County and 174 in Suffolk County), was monitored for carbon monoxide concentrations during the winter of 1986 (Research Triangle Institute, 1990). In this study, four combustion sources were examined: gas cooking appliances, unvented kerosene space heaters, wood-burning stoves and fireplaces and tobacco products.

Gas ranges and kerosene heaters were found to result in small increases in average carbon monoxide levels. Use of a wood-burning stove or fireplace resulted in lower average carbon monoxide levels, presumably owing to increased air exchange rates associated with use. The study found no effect on average carbon monoxide levels with tobacco combustion and no difference by location in the residence.

Koontz & Nagda (1987), utilizing census data for sample selection, monitored 157 homes in 16 neighbourhoods in north-central Texas, USA, over a 9-week period between January and March 1985. Unvented gas space heaters were used as the primary means of heating in 82 residences (13 had one unvented gas space heater, 36 had two, and 33 had three or more) and as a secondary heat source in
29 residences (17 had one unvented gas space heater, and 12 had two or more).

Residences in which unvented gas space heaters are the primary heat source exhibited the highest carbon monoxide concentrations. Carbon monoxide concentrations were greater than or equal to 10 mg/m$^3$ (9 ppm) in 12% of the homes, with the highest concentration measured at 41.9 mg/m$^3$ (36.6 ppm). No values were measured above 10 mg/m$^3$ (9 ppm) for residences in which an unvented gas space heater was not used at all or was used as a secondary heat source. Five of the residences exceeded the 1-h, 40 mg/m$^3$ (35 ppm) level, whereas seven of the residences exceeded the 8-h, 10 mg/m$^3$ (9 ppm) level. Higher carbon monoxide levels were associated with maltuned unvented gas appliances and the use of multiple unvented gas appliances.

In a study of 14 homes with one or more unvented gas space heaters (primary source of heat) in the area of Atlanta, Georgia, USA, McCarthy et al. (1987) measured carbon monoxide levels by continuous NDIR monitors in two locations in the homes (room with the heater and a remote room in the house) and outdoors. One out of the 14 unvented gas space heater homes exceeded 10 mg/m$^3$ (9 ppm) during the sampling period. Mean indoor values ranged from 0.30 to 10.87 mg/m$^3$ (0.26 to 9.49 ppm) and varied as a function of the use pattern of the heater. Only one of the homes used more than one heater during the air sampling. Outdoor concentrations ranged from 0.34 to 1.8 mg/m$^3$ (0.3 to 1.6 ppm).

Investigations of indoor air pollution by different heating systems in 16 private houses in Germany (Moriske et al., 1996) showed carbon monoxide concentrations up to 16 mg/m$^3$ (14 ppm) (98th percentile) during the heating period and up to 4.6 mg/m$^3$ (4.0 ppm) during the non-heating period in 8 homes with coal burning and open fireplace. In 8 homes with central heating, carbon monoxide concentrations were up to 2.3 mg/m$^3$ (2.0 ppm) during both heating and non-heating periods. In a home on the ground floor of a block of flats with a central stove in the basement below, carbon monoxide concentrations were up to 64 mg/m$^3$ (56 ppm) during the heating season.
2) Peak indoor-source-related concentrations

Short-term or peak indoor carbon monoxide concentrations associated with specific sources were obtained for a few field studies. In these studies, a wide range of peak carbon monoxide concentrations was observed in various residences with different indoor carbon monoxide sources. The highest concentrations measured (>700 mg/m³ [>600 ppm]) were associated with emissions from geysers (water heaters), found in a large study conducted in the Netherlands (Brunekreef et al., 1982). Peak levels of carbon monoxide associated with gas ranges were from 1.1 mg/m³ (1.0 ppm) to more than 110 mg/m³ (100 ppm). This broad range is somewhat consistent with the results of other studies evaluating carbon monoxide emissions from gas ranges. The variability is in part due to the number of burners used, flame condition, condition of the burners, etc. As might be expected, radiant kerosene heaters produced higher carbon monoxide concentrations than did convective heaters. Unvented gas space heaters were generally associated with higher carbon monoxide peaks than were gas ranges or kerosene heaters. As noted above, the peaks associated with gas or kerosene heaters are likely to be sustained over longer periods of time because of the long source-use times.

Test houses have been used by investigators to evaluate the impact of specific sources, modifications to sources and variations in their use on residential peak carbon monoxide concentrations.

In one of the earliest investigations of indoor air quality, Wade et al. (1975) measured indoor and outdoor carbon monoxide levels in four houses that had gas stoves. Indoor concentrations were found to be 1.7–3.8 times higher than the outdoor levels. Carbon monoxide levels in one house exceeded 10 mg/m³ (9 ppm), the NAAQS reference level. As part of a modelling study of emissions from a gas range, Davidson et al. (1987) measured carbon monoxide concentrations in three residences. Peak carbon monoxide levels in excess of 6 mg/m³ (5 ppm) were measured in one townhouse.

Indoor carbon monoxide levels associated with wood-burning stoves were measured in two test house studies. In one study (Humphreys et al., 1986), indoor carbon monoxide levels associated with the use of both airtight (conventional and catalytic) and non-airtight wood heaters were evaluated in a 337-m³ weatherized home. Indoor carbon monoxide concentrations were higher than outdoor
levels for all tests. Conventional airtight stoves produced indoor carbon monoxide levels typically about 1.1–2.3 mg/m³ (1–2 ppm) above background level, with a peak concentration of 10.4 mg/m³ (9.1 ppm). Use of non-airtight stoves resulted in average indoor carbon monoxide concentrations 2.3–3.4 mg/m³ (2–3 ppm) above outdoor concentrations, with peak concentrations as high as 33.9 mg/m³ (29.6 ppm). In a 236-m³ house (Traynor et al., 1984), four wood-burning stoves (three airtight and one non-airtight) were tested. The airtight stoves generally resulted in small contributions to both average and peak indoor carbon monoxide levels (0.11–1.1 mg/m³ [0.1–1 ppm] for the average and 0.23–3.1 mg/m³ [0.2–2.7 ppm] for the peak). The non-airtight stove contributed as much as 10.4 mg/m³ (9.1 ppm) to the average indoor level and 49 mg/m³ (43 ppm) to the peak.

3) Indoor concentrations related to environmental tobacco smoke

Carbon monoxide has been measured extensively in chamber studies as a surrogate for environmental tobacco smoke (e.g., Bridge & Corn, 1972; Hoegg, 1972; Weber et al., 1976, 1979a,b; Leaderer et al., 1984; Weber, 1984; Clausen et al., 1985). Under steady-state conditions in chamber studies, where outdoor carbon monoxide levels are monitored and the tobacco brands and smoking rates are controlled, carbon monoxide can be a reasonably good indicator of environmental tobacco smoke and is used as such. Under such chamber conditions, carbon monoxide concentrations typically range from less than 1.1 mg/m³ (1 ppm) to greater than 11 mg/m³ (10 ppm).

A number of field studies have monitored carbon monoxide in different indoor environments with and without smoking occupants. Although carbon monoxide concentrations were generally higher in indoor spaces when smoking occurred, the concentrations were highly variable. The variability of carbon monoxide production from tobacco combustion, the variability in the number of cigarettes smoked and differences in ventilation and variability of outdoor concentrations make it difficult to assess the contribution of tobacco combustion to indoor carbon monoxide concentrations. The chamber studies and field studies conducted do indicate that under typical smoking conditions encountered in residences or offices, carbon monoxide concentrations can be expected to be above background outdoor levels, but lower than the levels resulting from other unvented combustion sources. In indoor spaces where heavy smoking occurs and in small
indoor spaces, carbon monoxide emissions from tobacco combustion will be an important contributor to carbon monoxide concentrations.

5.7 Occupational exposure

Carbon monoxide is a ubiquitous contaminant occurring in a variety of occupational settings. The number of persons occupationally exposed to carbon monoxide in the working environment is greater than for any other physical or chemical agent (Hosey, 1970), with estimates as high as 975 000 occupationally exposed at high levels in the USA (NIOSH, 1972).

Two main sources for background exposures in both occupational and non-occupational settings appear to be smoking and the internal combustion engine (NAS, 1969). Also, endogenous carbon monoxide may be derived from certain halomethanes that are biotransformed by mixed-function oxidases in vivo. Smoking is a personal habit that must be considered in evaluating exposure in general, as well as those occurring in workplaces. In addition, work environments are often located in densely populated areas, and such areas frequently have a higher background concentration of carbon monoxide compared with less densely populated residential areas. Thus, background exposures may be greater during work hours than during non-work hours.

There are several sources other than smoking and the internal combustion engine that contribute to exposure during work hours. These include contributions to background levels by combustion of organic materials in the geographic area of the workplace; work in specific industrial processes that produce carbon monoxide; and exposure to halomethanes that give rise to endogenous carbon monoxide during biotransformation. Therefore, a number of potential sources of carbon monoxide should be considered when evaluating the risk associated with carbon monoxide exposure, including personal habits, living conditions and co-exposure to other potential sources of carbon monoxide or to xenobiotics that are metabolized to carbon monoxide or that interfere with biotransformation processes. Finally, the particular vulnerability of specific groups at increased risk because of some physiological (pregnancy) or pathological (angina, anaemia, respiratory insufficiency) conditions should be taken into account in the health surveillance of occupationally exposed workers.
5.7.1 **Occupational exposure limits**

Elevated concentrations of carbon monoxide occur in numerous settings, including those at work, at home or in the street. Acute effects related to production of anoxia from exposures to carbon monoxide have historically been a basis for concern. In recent years, however, this concern has grown to include concerns for potential effects from chronic exposure as well (Sammons & Coleman, 1974; Rosenstock & Cullen, 1986a,b).

Three kinds of occupational exposure limits are currently utilized in a number of countries (Table 12). The most common are average permissible concentrations for a typical 8-h working day (time-weighted average, TWA), concentrations for short-term exposures, generally of 15-min duration (short-term exposure limit, STEL), and maximum permissible concentrations not to be exceeded (ceiling limit).

Whereas some countries do not apply legally binding occupational exposure limits and others refer to maximum allowable concentrations, threshold limit values (TLVs) are the most widely used and accepted standards representing “conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects.” In the introduction to the list of TLVs published by the American Conference of Governmental Industrial Hygienists (ACGIH, 1995), it is also stressed that these limits are not fine lines separating safe from dangerous situations, but rather guidelines to be used by professionals with a specific training in industrial hygiene. Moreover, it is recognized that a small percentage of workers may be “unusually responsive to some industrial chemicals because of genetic factors, age, personal habits (smoking, alcohol, or other drugs), medication, or previous exposure. Such workers may not be adequately protected from adverse health effects at concentrations at or below the threshold limit. An occupational physician should evaluate the extent to which such workers require additional protection” (ACGIH, 1995).

A TWA concentration of 29 mg/m³ (25 ppm) has been recommended by ACGIH as the TLV for carbon monoxide since 1991. Such
### Table 12. Worldwide occupational exposure limits for carbon monoxide\(^a\)

<table>
<thead>
<tr>
<th>Country</th>
<th>TWA mg/m(^3)</th>
<th>TWA ppm</th>
<th>STEL mg/m(^3)</th>
<th>STEL ppm</th>
<th>Ceiling mg/m(^3)</th>
<th>Ceiling ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria</td>
<td>33</td>
<td>30</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Belgium</td>
<td>55</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Brazil</td>
<td>43</td>
<td>39</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>20</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Chile</td>
<td>44</td>
<td>40</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>China, P.R. of</td>
<td>30</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>China (Taiwan)</td>
<td>55</td>
<td>50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Czechoslovakia</td>
<td>30</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>150</td>
<td>–</td>
</tr>
<tr>
<td>Denmark</td>
<td>40</td>
<td>35</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Egypt</td>
<td>–</td>
<td>100</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Finland</td>
<td>55</td>
<td>50</td>
<td>85</td>
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\(^a\) From ACGIH (1987); CEC (1993).
a limit is likely to be adopted by other countries traditionally relying on ACGIH-recommended TLVs and by countries relying on the recommended exposure limits (RELs) adopted by the US National Institute for Occupational Safety and Health (NIOSH), currently set at 40 mg/m$^3$ (35 ppm). Although ceiling limits and STELs are not expressly indicated, general rules advise that exposure levels “may exceed the TLV-TWA three times for no more than 30 min during a work-day, and under no circumstances should they exceed five times the TLV-TWA.” Therefore, a ceiling of 143 mg/m$^3$ (125 ppm) and a STEL of 86 mg/m$^3$ (75 ppm) may be derived from such a guidance. Biotransformation into carbon monoxide rather than other toxic properties is the scientific basis for setting the TLV for methylene chloride at 177 mg/m$^3$ (50 ppm).

In addition to ambient monitoring, biomarkers can be used to assess exposure, susceptibility and early effects. Carboxyhaemoglobin is a widely accepted biomarker — or biological exposure index (BEI), according to ACGIH nomenclature — of exposure to carbon monoxide. The ACGIH has recently proposed a carboxyhaemoglobin level of 3.5% as a BEI being most likely reached by a non-smoker at the end of an 8-h exposure to 29 mg carbon monoxide/m$^3$ (25 ppm) (ACGIH, 1991). The biological tolerance limit (BAT) recommended by the DFG (1996) is 5% carboxyhaemoglobin, corresponding to a carbon monoxide TWA level of 34 mg/m$^3$ (30 ppm).

Neither the BEI nor the BAT is applicable to tobacco smokers. According to Gilli et al. (1979), a serum thiocyanate level above 3.8 mg/litre and a carboxyhaemoglobin level in the range of 2.5–6% are a certain indication of cigarette smoking, whereas a thiocyanate concentration below 3.8 mg/litre and a carboxyhaemoglobin level above 5% indicate occupational exposure to carbon monoxide. Tobacco smoking can also be assessed measuring cotinine excretion, but studies relating cotinine in urine to carboxyhaemoglobin are not available. An alternative BEI is carbon monoxide concentration in end-expired air collected at the end of the working shift. A concentration of 23 mg/m$^3$ (20 ppm) would be reached after exposure to an 8-h TWA level of 29 mg/m$^3$ (25 ppm).

It ought to be noted that both BEIs and BATs are usually established taking into account the relationship between biomarkers and exposure levels rather than the relationship between biomarkers and adverse effects. Therefore, higher carboxyhaemoglobin levels are generally accepted for smokers, taking into account the fact that their higher levels result from a voluntary habit giving rise to an additional
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carbon monoxide burden. However, if adverse effects are expected to occur as a consequence of carboxyhaemoglobin and carbon monoxide body burden, then smokers should be advised about their additional risk.

NIOSH (1972) observed that “the potential for exposure to carbon monoxide for employees in the work place is greater than for any other chemical or physical agent” and recommended that exposure to carbon monoxide be limited to a concentration no greater than 40 mg/m$^3$ (35 ppm), expressed as a TWA for a normal 8-h workday, 5 days per week. A ceiling concentration was also recommended at a limit of 230 mg/m$^3$ (200 ppm), not to exceed an exposure time greater than 30 min. Occupational exposures at the proposed concentrations and conditions underlying the basis of the standard were considered to maintain carboxyhaemoglobin in blood below 5%.

Although it was not stated, the basis of the recommended NIOSH standard (i.e., maintaining carboxyhaemoglobin below 5% in blood) assumes that (1) the sensitive population group protected by air quality standards would not be occupationally exposed and (2) contributions from other non-occupational sources would also be less than a TWA concentration of 40 mg/m$^3$ (35 ppm). It was recognized that such a standard may not provide the same degree of protection to smokers, for example. Other particularly vulnerable groups of workers deserve special consideration. Among these, pregnant women should require special protection because of the potentially deleterious effects of carbon monoxide exposure on the fetuses (NIOSH, 1972). The same requirement for safety of pregnant women has been established by the DFG (1996).

Although recognizing that biological changes might occur at the low level of exposure recommended in the proposed standard, NIOSH concluded that subtle aberrations in the nervous system with exposures producing carboxyhaemoglobin concentrations in blood at or below 5% did not demonstrate significant impairments that would cause concern for the health and safety of workers. In addition, NIOSH observed that individuals with impairments that interfere with normal oxygen delivery to tissues (e.g., emphysema, anaemia, coronary heart disease) may not have the same degree of protection as have less impaired individuals. It was also recognized that work at higher altitudes (e.g., 1500–2400 m above sea level) would necessitate
decreasing the exposure limit below 40 mg/m³ (35 ppm), to compensate for a decrease in the oxygen partial pressure as a result of high-altitude environments and a corresponding decrease in oxygenation of the blood (NIOSH, 1972). High-altitude environments of concern include airline cabins at a pressure altitude of 1500 m or greater (NRC, 1986b) and high mountain tunnels (Miranda et al., 1967).

5.7.2 Exposure sources

The contribution of occupational exposures to carbon monoxide can be separated from other sources of carbon monoxide exposure, but there are at least two conditions to consider:

(1) When carbon monoxide concentrations at work are higher than the carbon monoxide equilibrium concentration associated with the percent carboxyhaemoglobin at the start of the work shift, there will be a net absorption of carbon monoxide and an increase in percent carboxyhaemoglobin. Non-smokers will show an increase that is greater than that for smokers because they start from a lower baseline carboxyhaemoglobin level. In some cases, non-smokers may show an increase and smokers a decrease in percent carboxyhaemoglobin.

(2) When carbon monoxide concentrations at work are lower than the equilibrium concentration necessary to produce the worker’s current level of carboxyhaemoglobin, then the percent carboxyhaemoglobin will show a decrease. There will be a net loss of carbon monoxide at work.

As mentioned above, occupational exposures can stem from three sources: (1) through background concentrations of carbon monoxide, (2) through work in industrial processes that produce carbon monoxide as a product or by-product and (3) through exposure to some halomethanes that are metabolized to carbon monoxide \textit{in vivo}. In addition, work environments that tend to accumulate carbon monoxide concentrations may result in occupational exposures. Rosenman (1984) lists a number of occupations in which the workers may be exposed to high carbon monoxide concentrations. This list includes acetylene workers, blast furnace workers, coke oven workers, diesel engine operators, garage mechanics, steel workers, metal oxide...
reducers, miners, nickel refining workers, organic chemical synthesizers, petroleum refinery workers and pulp and paper workers. In addition, because methylene chloride is metabolized to carbon monoxide in the body, aerosol packagers, anaesthetic makers, bitumen makers, degreasers, fat extractors, flavouring makers, leather finish workers, oil processors, paint remover makers, resin makers and workers exposed to dichloromethane-containing solvent mixtures and stain removers can also have high carboxyhaemoglobin levels.

5.7.3 Combined exposure to xenobiotics metabolized to carbon monoxide

Certain halomethanes, particularly dichloromethane, a frequently used organic solvent also known as methylene chloride (reviewed in EHC 164), are metabolized to carbon monoxide, carbon dioxide and chlorine (or iodine or bromine) in a reaction catalysed by cytochrome P-450 2E1.

Combined exposures frequently occur at the workplace, and their temporal sequence may result in opposite effects. Concurrent exposure to other substrates of cytochrome P-450 2E1 — including ethanol and a number of common organic solvents, such as benzene and its alkyl derivatives, trichloroethylene and acetone — may cause a competitive inhibition of the oxidation of methylene chloride to carbon monoxide. As the same substances may act as inducers, provided they are no longer present to compete with methylene chloride, increased rates of carbon monoxide formation are expected to occur in people chronically exposed to such solvents or to ethanol and then exposed to methylene chloride at the workplace. As a corollary of these observations, and taking into account the fact that the carbon monoxide produced from inhaled dichloromethane rather than the parent compound underlies non-cancer end-points and the fact that the carbon monoxide formation rate is modified in a different way by prior and concurrent exposure to other substances, it would seem logical to rely on the same BEIs proposed for carbon monoxide to monitor exposure to methylene chloride and other halomethanes rather than on ambient monitoring alone.

5.7.4 Typical studies at the workplace

Aircraft accidents involving 113 aircraft, 184 crew members and 207 passengers were investigated to characterize accident toxicology
and to aid in the search for causation of a crash (Blackmore, 1974). Determinations of percent carboxyhaemoglobin in blood samples obtained from victims enabled differentiation of a variety of accident sequences involving fires. For example, percent carboxyhaemoglobin determinations combined with passenger seating information and crew assignments can help differentiate between fire in flight and fire after the crash, between survivability of the crash and death due to smoke inhalation, and between specific malfunctions in equipment operated by a particular crew member and defects in space heating in the crew cabin or passenger compartment. One accident in the series was associated with a defective space heater in the crew compartment. Another accident was also suspicious with regard to a space heater.

Carbon monoxide concentrations were used to classify workers from 20 foundries into three groups: those with definite occupational exposure, those with slight exposure and controls (Hernberg et al., 1976). Angina pectoris, electrocardiogram findings and blood pressures of foundry workers were evaluated in terms of carbon monoxide exposure for the 1000 workers who had the longest occupational exposures for the 20 foundries. Angina showed a clear dose-response with exposure to carbon monoxide either from occupational sources or from smoking, but there was no such trend in electrocardiogram findings. The systolic and diastolic pressures of carbon monoxide-exposed workers were higher than those for other workers, when age and smoking habits were considered.

Carboxyhaemoglobin and smoking habits were studied for a population of steelworkers and compared with those for blast furnace workers as well as employees not exposed at work (Jones & Walters, 1962). Carbon monoxide is produced in coke ovens, blast furnaces and sintering operations. Exhaust gases from these operations are often used for heating and as fuels for other processes. Fifty-seven volunteers working in the blast furnace area were studied for smoking habits, symptoms of carbon monoxide exposure and estimations of carboxyhaemoglobin levels by an expired air technique. The main increase in carboxyhaemoglobin for blast furnace personnel was 2.0% for both smokers and non-smokers in the group. For smokers in the unexposed control group, there was a decrease in percent carboxyhaemoglobin. A follow-up study found similar results (Butt et al., 1974). Virtamo & Tossavainen (1976) reported a study of carbon monoxide measurements in air of 67 iron, steel or copper alloy
foundries. Blood carboxyhaemoglobin of iron workers exceeded 6% in 26% of the non-smokers and 71% of the smokers studied.

Poulton (1987) found that a medical helicopter with its engine running in a narrowed or enclosed helipad was a source of potential exposure to carbon monoxide, JP-4 fuel and possibly other combustion products for flight crews, medical personnel, bystanders and patients being evacuated. Measurements were made by means of a portable infrared analyser. Carbon monoxide concentrations were found to be greatest near the heated exhaust. Concentrations ranged from 9 to 49 mg/m$^3$ (8 to 43 ppm).

Exhaust from seven of the most commonly used chain-saws (Nilsson et al., 1987) was analysed under laboratory conditions to characterize emissions. The investigators conducted field studies on exposures of loggers using chain-saws in felling operations and also in limbing and bucking into lengths. In response to an inquiry, 34% of the loggers responded that they often experienced discomfort from the exhaust fumes of chain-saws, and another 50% complained of occasional problems. Sampling for carbon monoxide exposures was carried out for 5 days during a 2-week work period in a sparse pine stand at an average wind speed of 0–3 m/s, a temperature range of 1–16 °C and a snow depth of 50–90 cm. Carbon monoxide concentrations ranged from 10 to 23 mg/m$^3$ (9 to 20 ppm), with a mean value of 20.0 mg/m$^3$ (17.5 ppm). Carbon monoxide concentrations measured under similar, but snow-free, conditions ranged from 24 to 44 mg/m$^3$ (21 to 38 ppm), with a mean value of 32 mg/m$^3$ (28 ppm). In another study, carbon monoxide exposures were monitored for non-smoking chain-saw operators; average exposures recorded were from 23 to 63 mg/m$^3$ (20 to 55 ppm), with carboxyhaemoglobin levels ranging from 1.5 to 3.0% (Van Netten et al., 1987).

Forklift operators, stevedores and winch operators were monitored for carbon monoxide in expired air, using a Mine Safety Appliances analyser, to calculate percent carboxyhaemoglobin (Breyssse & Bovee, 1969). Periodic blood samples were collected to validate the calculations. Forklift operators and stevedores, but not winch operators, work in the holds of ships. The ships to be evaluated were selected on the basis of their use of gasoline-powered forklifts for operations. To evaluate seasonal variations in percent carboxyhaemoglobin, analyses were performed for one 5-day period per
month for a full year. Efforts were made to select a variety of ships for evaluation. In total, 689 determinations of percent carboxyhaemoglobin were made from samples of blood to compare with values from samples of expired air. The samples were collected on 51 separate days involving 26 different ships. Smoking was found to be a major contributing factor to the percent carboxyhaemoglobin levels found. Carboxyhaemoglobin values for non-smokers indicated that the use of gasoline-powered lifts in the holds of the ships did not produce a carbon monoxide concentration in excess of 57 mg/m$^3$ (50 ppm) for up to 8 h as a TWA under the work rules and operating conditions in practice during the study. Smoking behaviour confounded exposure evaluations.

Carbon monoxide concentrations have been measured in a variety of workplaces where potential exists for accumulation from outside sources. Exposure conditions in workplaces, however, are substantially different. The methods to be applied, group characteristics, jobs being performed, smoking habits and physical characteristics of the facilities themselves introduce considerable variety in the approaches used. Typical studies are discussed below.

Wallace (1983) investigated carbon monoxide in air and breath of employees working at various times over a 1-month period in an office constructed in an underground parking garage. Carbon monoxide levels were determined by use of a device containing a proprietary solid polymer electrolyte to detect electrons emitted in the oxidation of carbon monoxide to carbon dioxide. Variation in carbon monoxide measurements in ambient air showed a strong correlation with traffic activity in the parking garage. Initially, the office carbon monoxide levels were found to be at a daily average of 21 mg/m$^3$ (18 ppm), with the average from 12:00 to 4:00 p.m. at 25 mg/m$^3$ (22 ppm) and the average from 4:00 to 5:00 p.m. at 41 mg/m$^3$ (36 ppm). Analyses of expired air collected from a group of 20 non-smokers working in the office showed a strong correlation with concentrations of carbon monoxide in ambient air and traffic activity. For example, the average carbon monoxide in expired air for one series of measurements was 26.8 mg/m$^3$ (23.4 ppm), compared with simultaneous measurements of carbon monoxide concentrations in air of 25–30 mg/m$^3$ (22–26 ppm). After a weekend, carbon monoxide concentrations in breath on Monday morning were substantially decreased (around 8 mg/m$^3$ [7 ppm]), but they rose again on Monday afternoon to equal
the air levels of 14 mg/m$^3$ (12 ppm). Closing fire doors and using existing garage fans decreased carbon monoxide concentrations in the garage offices to 2.3 mg/m$^3$ (2 ppm) or less, concentrations similar to those for other offices in the complex that were located away from the garage area.

Carboxyhaemoglobin levels (Ramsey, 1967) were determined over a 3-month period during the winter for 38 parking garage attendants, and the values for carboxyhaemoglobin were compared with values from a group of 27 control subjects. Blood samples were collected by finger stick on Monday mornings at the start of the work week, at the end of the work shift on Mondays and at the end of the work week on Friday afternoons. Hourly analyses were carried out on three different weekdays using potassium paladosulfite indicator tubes for the concentrations of carbon monoxide at three of the six garages in the study. Hourly levels ranged from 8 to 270 mg/m$^3$ (7 to 240 ppm), and the composite mean of the 18 daily averages was 67.4 ± 28.5 mg/m$^3$ (58.9 ± 24.9 ppm). Although the Monday versus Friday afternoon values for carboxyhaemoglobin were not significantly different, there were significant differences between Monday morning and Monday afternoon values. Smokers showed higher starting baseline levels, but there was no apparent difference in net increase in carboxyhaemoglobin body burden between smokers and non-smokers. Carboxyhaemoglobin levels for non-smokers ranged from a mean of 1.5 ± 0.83% for the morning samples to 7.3 ± 3.46% for the afternoon samples. For smokers, these values were 2.9 ± 1.88% for the morning and 9.3 ± 3.16% for the afternoon. The authors observed a crude correlation between daily average carbon monoxide levels in air and carboxyhaemoglobin levels observed for a 2-day sampling period.

In a study of motor vehicle examiners conducted by NIOSH (Stern et al., 1981), carbon monoxide levels of 5–24 mg/m$^3$ (4–21 ppm) TWA were recorded in six outdoor motor vehicle inspection stations. In contrast, the semi-open and enclosed stations had levels of 11–46 mg/m$^3$ (10–40 ppm) TWA. The levels exceeded the recommended NIOSH standard of 40 mg/m$^3$ (35 ppm) TWA on 10% of the days sampled. In addition, all stations experienced peak short-term levels above 230 mg/m$^3$ (200 ppm).
Carboxyhaemoglobin levels were measured for 22 employees of an automobile dealership during the winter months when garage doors were closed and ceiling exhaust fans were turned off (Andreics et al., 1979). Employees subjected to testing included garage mechanics, secretaries and sales personnel. These included 17 males aged 21–37 and five females aged 19–36. Blood samples were collected on a Monday morning before the start of work and on Friday at the end of the work week. Smokers working in the garage area showed a Monday morning mean carboxyhaemoglobin value of 4.87 ± 3.64% and a Friday afternoon mean value of 12.9 ± 0.83%. Non-smokers in the garage showed a corresponding increase in carboxyhaemoglobin, with a Monday morning mean value of 1.50 ± 1.37% and a Friday afternoon mean value of 8.71 ± 2.95%. Non-smokers working in areas other than the garage had a Friday afternoon mean value of 2.38 ± 2.32%, which was significantly lower than the mean values for smokers and non-smokers in the garage area. Environmental concentrations or breathing zone samples for carbon monoxide were not collected. The authors concluded that smokers have a higher baseline level of carboxyhaemoglobin than do non-smokers, but both groups show similar increases in carboxyhaemoglobin during the work week while working in the garage area. The authors observed that the concentrations of carboxyhaemoglobin found in garage workers were the same as those reported to produce neurological impairment. These results are consistent with those reported by Amendola & Hanes (1984), who reported some of the highest indoor levels collected at automobile service stations and dealerships. Concentrations ranged from 18.5–126.9 mg/m³ (16.2–110.8 ppm) in cold weather to 2.5–24.7 mg/m³ (2.2–21.6 ppm) in warm weather.

A group of 34 employees, 30 men and 4 women, working in multistorey garages was evaluated for exposures to exhaust fumes (Fristedt & Akesson, 1971). Thirteen were service employees working at street level, and 21 were shop employees working either one storey above or one storey below street level. Six facilities were included in the study. Blood samples were collected on a Friday at four facilities, on Thursday and Friday at another and on a Thursday only at a sixth facility. The blood samples were evaluated for red blood cell and white blood cell counts, carboxyhaemoglobin, lead and δ-amino-levulinic acid. Work histories, medical case histories and smoking habits were recorded. Among the employees evaluated, 11 of 24 smokers and 3 of 10 non-smokers complained of discomfort from
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exhaust fumes. Smokers complaining of discomfort averaged 6.6% carboxyhaemoglobin, and non-smokers complaining averaged 2.2% carboxyhaemoglobin. The corresponding values for non-complaining workers averaged 4.2 and 1.1%, respectively.

Air pollution by carbon monoxide in underground garages was investigated as part of a larger study of traffic pollutants in Paris, France (Chovin, 1967). Work conducted between the hours of 8:00 a.m. and 10:00 p.m. resulted in exposures in excess of 57 mg/m$^3$ (50 ppm) and up to 86 mg/m$^3$ (75 ppm), on a TWA basis.

As part of a larger study of carbon monoxide concentrations and traffic patterns in Paris (Chovin, 1967), samples were taken in road tunnels. There was good correlation between the traffic volumes combined with the lengths of the tunnels and the carbon monoxide concentrations found. None of the tunnels studied had mechanical ventilation. The average carbon monoxide concentrations in the tunnels were 31 mg/m$^3$ (27 ppm) and 34 mg/m$^3$ (30 ppm) for 1965 and 1966, respectively, compared with an average of 27 mg/m$^3$ (24 ppm) in the streets for both years. The average risk for a person working or walking in a street or tunnel was considered by the authors to be 3–4 times less than the maximal risk indicated by values for carbon monoxide from instantaneous air sample measurements. In the USA, Evans et al. (1988) studied bridge and tunnel workers in metropolitan New York City, New York. The average carboxyhaemoglobin concentration over the 11 years of study averaged 1.73% for non-smoking bridge workers and 1.96% for tunnel workers.

In a discussion of factors to consider in carbon monoxide control of high-altitude highway tunnels, Miranda et al. (1967) reviewed the histories of several tunnels. Motor vehicles were estimated to emit about 0.03 kg carbon monoxide/km at sea level. At 3350 m and a grade of 1.64%, emissions were estimated at 0.1 kg/km (for vehicles moving upgrade). Tunnels with ventilation are generally designed to control carbon monoxide concentrations at or below 110 mg/m$^3$ (100 ppm). The Holland Tunnel in New York was reported to average 74 mg/m$^3$ (65 ppm), with a recorded maximum of 418 mg/m$^3$ (365 ppm) due to a fire. For the Sumner Tunnel in Boston, Massachusetts, ventilation is started at carbon monoxide concentrations of 110 mg/m$^3$ (100 ppm), and additional fans are turned on and an alarm is sounded at 290 mg/m$^3$ (250 ppm). The average carbon monoxide
concentration is 57 mg/m$^3$ (50 ppm). The Mont Blanc Tunnel is 11.6 km long at an average elevation of 1274 m. This tunnel is designed to maintain carbon monoxide concentrations at or below 110 mg/m$^3$ (100 ppm). The Grand Saint Bernard Tunnel is 5.6 km long at an average elevation of 1830 m. The tunnel is designed to maintain carbon monoxide concentrations at or below 230 mg/m$^3$ (200 ppm). For the tunnel at 3350 m, the authors recommended maintaining carbon monoxide concentrations at or below 29 mg/m$^3$ (25 ppm) for long-term exposures and at or below 57 mg/m$^3$ (50 ppm) for peaks of 1-h exposure. The recommendations are based on considerations of a combination of hypoxia from lack of oxygen due to the altitude and stress of carbon monoxide exposures of workers and motorists.

Carbon monoxide exposures of tollbooth operators were studied along the New Jersey, USA, Turnpike. The results reported by Heinold et al. (1987) indicated that peak exposures for 1 h ranged from 14 to 27 mg/m$^3$ (12 to 24 ppm), with peak 8-h exposures of 7–17 mg/m$^3$ (6–15 ppm).

Carboxyhaemoglobin levels were determined for 15 non-smokers at the start, middle and end of a 40-day submarine patrol (Bondi et al., 1978). Values found were 2.1%, 1.7% and 1.7%, respectively. The average carbon monoxide concentration in ambient air was 8 mg/m$^3$ (7 ppm). The authors observed that the levels of percent carboxyhaemoglobin found would not cause significant impairment of the submariners.

In contrast, Iglewicz et al. (1984) found in a 1981 study that carbon monoxide concentrations inside ambulances in New Jersey were often above the US EPA 8-h standard of 10 mg/m$^3$ (9 ppm). For example, measurements made at the head of the stretcher exceeded 10 mg/m$^3$ (9 ppm) on nearly 27% of the 690 vehicles tested, with 4.2% (29 vehicles) exceeding 40 mg/m$^3$ (35 ppm).

Environmental tobacco smoke has been reviewed (NRC, 1986b) for contributions to air contaminants in airliner cabins and to potential exposures for passengers and flight crew members. Environmental tobacco smoke is described as a complex mixture containing many components. Analyses of carbon monoxide content and particulate matter in cabin air were used as surrogates for the
vapour phases and solid components of environmental tobacco smoke, respectively. A mathematical model was developed and used to calculate the dilution of contaminants by outside make-up air. The amount of carbon monoxide in the cabin environment depends on the rate and number of cigarettes smoked and on the rate of dilution by outside make-up air. An additional factor to consider is the influence of pressure altitude on the absorption of carbon monoxide and other gases. The legal limit for pressure altitude is 2440 m. The partial pressure of oxygen is 16 kPa assuming 20% oxygen in the cabin air, compared with 20 kPa at sea level. It is possible that the absorption rate for carbon monoxide would be increased under hypobaric conditions.

A study of municipal bus drivers in the San Francisco Bay, California, USA, area by Quinlan et al. (1985) showed a TWA of 1.1–26 mg/m$^3$ (1–23 ppm), with a mean TWA of 6.3 mg/m$^3$ (5.5 ppm) and standard deviation of 5.6 mg/m$^3$ (4.9 ppm). The peak exposures ranged from 8 to 54 mg/m$^3$ (7 to 47 ppm), with a mean of 29.0 mg/m$^3$ (25.3 ppm) and standard deviation of 14.3 mg/m$^3$ (12.5 ppm).

Cooke (1986) reported finding no significant increases outside normal ranges, compared with the general population, for levels of blood lead and carboxyhaemoglobin in a group of 13 roadside workers. Samples were collected in the afternoon of a workday. Among the subjects, 7 of 13 were smokers and showed percent carboxyhaemoglobin in blood ranging from 3.0 to 8.8% (mean of 5.5%). For non-smokers, percent carboxyhaemoglobin ranged from 0.5 to 1.4% (mean of 1.2%). Each smoker had smoked at least one cigarette in the 4 h preceding collection of blood samples. No samples were collected before the start of work, and no measurements of carbon monoxide in air at the work sites were presented.