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Atmospheric Chemistry

Formaldehyde in the Ambient Atmosphere: From an Indoor Pollutant to an Outdoor Pollutant?

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atmospheric chemistry · biofuels · formaldehyde · indoor guideline values · indoor/outdoor relation

Formaldehyde has been discussed as a typical indoor pollutant for decades. Legal requirements and ever-lower limits for formaldehyde in indoor air have led to a continual reduction in the amount of formaldehyde released from furniture, building materials, and household products over many years. Slowly, and without much attention from research on indoor air, a change of paradigm is taking place, however. Today, the formaldehyde concentrations in outdoor air, particularly in polluted urban areas, sometimes already reach indoor levels. This is largely a result of photochemical processes and the use of biofuels. In the medium term, this development might have consequences for the way buildings are ventilated and lead to a change in the way we evaluate human exposure.

1. Introduction

Just a short time after Butlerow had discovered formaldehyde in 1855 and its first synthesis by von Hofmann in 1867, its potential applications were recognized. With Baekeland's patent in 1907, a duroplastic on the basis of phenol–formaldehyde became available to industry under the name "Bakelite".[1] In 1931, IG Farben brought Kaurit glue onto the market. This was based on formaldehyde and urea. The suitability of the low-cost urea–formaldehyde resins for bonding wood significantly contributed to the popularity of particleboard.[2] Formaldehyde's properties as a preservative and disinfectant were also recognized by Isaak and Ferdinand Blum at the end of the 19th century.[3] Today, formaldehyde is one of the most important industrial organic base chemicals and the worldwide production capacity is over 30 million tons per year.[4]

Formaldehyde became known as an indoor air pollutant in 1962 following a publication by Wittmann[5] in which he described the postmanufacture release of formaldehyde from particleboard. However, it took 15 more years before the German health authorities made the recommendation not to exceed an indoor formaldehyde concentration of 0.1 ppm.[*] Over the years, the indoor limit was reduced again and again by international committees, particularly following formaldehyde's classification as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC).[6] The currently lowest guideline values were published by the California Air Resources Board (CARB) at 3 $\mu g\,m^{-3}$ (2 ppb) as the Chronic Reference Exposure Limit (REL) and by the Agence Francaise de Sécurité Sanitaire de l'Environnement et du Travail (AFSSET) at 10 $\mu g\,m^{-3}$ (8 ppb) as a value for long-term exposure.[7] On the basis of two evaluations[8] the World Health Organization (WHO) considers an indoor value of 0.1 $mg\,m^{-3}$ (80 ppb) as sufficient.[9]

With the intensive discussion concerning formaldehyde as an indoor pollutant, it is difficult to understand why formaldehyde in the outdoor air is hardly taken into account by administrative bodies even though atmospheric scientists early identified formaldehyde as a designated HAP/TAC (hazardous air pollutant/toxic air contaminant)[10] and reported high formaldehyde concentrations in many environments years ago.[11] Kohse-Höinghaus et al.[12] have shown that formaldehyde is one primary product of the combustion of biofuels. Photochemical oxidation of precursor molecules is known as a secondary source of formaldehyde.[13] It can therefore be expected that, primarily in high-traffic metropolitan areas and photosmog regions, formaldehyde concen-

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[*] In the literature, the units "ppm" and "$\mu g\,m^{-3}$" are both used. All the measurement values given in this paper have been converted to "ppm" or "ppb" (1 $\mu g\,m^{-3} = 0.815$ ppb at 293 K and 1013 mbar, and with $M_{HCHO} = 30.03\ g\,mol^{-1}$).

trations will remain at elevated levels or even continue to rise in the coming years. In contrast to this trend, the formaldehyde emission indoors will continue to sink. This paper summarizes the current knowledge on the topic of "formaldehyde in ambient air". It shows that a balanced evaluation of human exposure is possible only when both indoor and outdoor air is considered.

2. Formaldehyde Properties and Analysis

2.1. Formaldehyde Properties

Formaldehyde (CAS No. 50-000-0) is a planar molecule, which is gaseous at ambient conditions, highly reactive, and soluble in water, alcohol, acetone, and ether (boiling point: $-21\,^{\circ}\mathrm{C}$; dipole moment: 2.33 D: $\log(K_{\mathrm{OW}})$: -0.83; Henry's law constant: $2.5\times10^{3}\,\mathrm{M\,atm^{-1}}$ at $25\,^{\circ}\mathrm{C}$).[14]

The high solubility of formaldehyde in water causes rapid absorption in the respiratory and gastrointestinal tract. As an electrophile, formaldehyde can react with nucleophilic biogenic compounds in the body. The lowest observable adverse effects levels (LOAEL) for human sensory irritation range from 0.4 ppm (rhinitis) to 3 ppm (eye, nasal, and throat irritation).[14] A recent study of formaldehyde and sensory irritation in humans showed that eye irritation is the most sensitive parameter. A no observed effect level (NOEL) of 0.5 ppm was derived in the case of constant exposure.[15] Wolkoff and Nielsen[8] have discussed the toxicological properties of formaldehyde. In the general population they consider the WHO guideline protective against both acute and chronic sensory irritation in the airways. Moreover, the same authors state that the WHO guideline value is also considered relevant for prevention of all types of cancer, including lymphohematopoietic malignancies.

2.2. Formaldehyde Analysis in Air

For the analysis of formaldehyde in air, spectroscopy techniques and derivatization methods, as recently reviewed by Salthammer et al.,[14] have been developed. In the indoor environment, the acetylacetone (acac) method and the 2,4-dinitrophenylhydrazine (DNPH) method are commonly applied.

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The acac method involves the cyclization of 2,4-pentanedione, ammonium acetate, and formaldehyde to form the dihydropyridine 3,5-diacetyl-1,4-dihydrolutidine (DDL). Sampling is carried out by passing air through an absorber where formaldehyde is trapped in distilled water. Quantification is usually performed by fluorescence at 510 nm with excitation at 412 nm; the limit of quantitation is 2 ppb for a sampling volume of 80 L.[16] Today, portable instruments are also available and enable reliable in situ measurement of formaldehyde on a timescale of seconds.[14,17]

In acidic solution, hydrazones are formed from DNPH by nucleophilic addition to the carbonyl group, followed by elimination of water. In sampling, air is pulled through cartridges typically containing silica gel coated with an acidic solution of DNPH. Chromatographic separation of the hydrazones is achieved by means of HPLC and water/acetonitrile solvent combinations with binary or ternary gradients. UV spectroscopy is used for detection. The limit of quantitation is 1 ppb for a sampling volume of 120 L.[16]

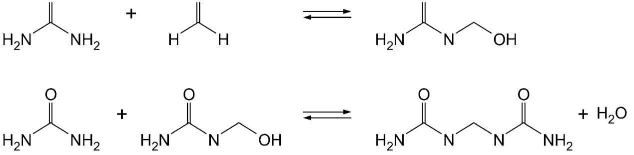
For measurements of atmospheric formaldehyde, the acac and the DNPH methods are routinely used, but differential optical absorption spectroscopy (DOAS), proton transfer reaction mass spectrometry (PTR-MS), and many other sensitive online techniques are also applied.[14] Wisthaler et al.[17] have compared the above-mentioned methods under simulated atmospheric conditions and report detection limits of 50 ppt (acac, online), 80 ppt (acac, sampling), 40 ppt (DNPH), 400 ppt (DOAS), and 200 ppt (PTR-MS). However, the PTR-MS method was found to be unsuitable for a humid indoor environment.[18]

3. Sources of Formaldehyde

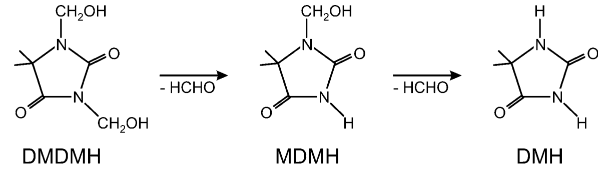
3.1. Indoor Sources

Wood-based materials used in construction or in furniture production have long been the typical indoor source. The reason for their subsequent and often long-lasting release of formaldehyde is generally the reversibility of the urea–formaldehyde (UF) reaction under the influence of moisture (Scheme 1). Wood products bonded with phenol–formaldehyde resins produce much lower emissions. Other building products such as floor coverings, UF spray foam, and mineral wool insulation can all release formaldehyde.

One use of dimethyloldimethyl hydantoin (DMDMH) is as a formaldehyde donor (Scheme 2) in cosmetics.[19] Increased concentrations can occur in combination with the use of formaldehyde as a preservative or disinfectant, for example



Scheme 1. The reversible reaction of urea and formaldehyde to form monomethylolurea and diureamethane.[2]

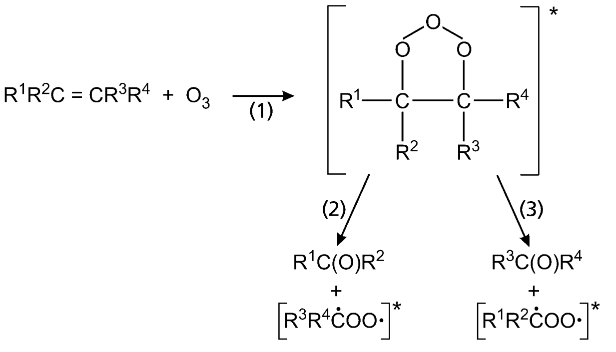


Scheme 2. The release of formaldehyde from dimethyloldimethyl hydantoin (DMDMH).[19a]

in museums[20] and in medical laboratories.[21] The significance of formaldehyde formation from chemical reactions in indoor areas was recognized by Weschler et al.[22] while investigating the effect of ozone on textile floor coverings. Wolkoff et al.[23] pointed out that the terpene/ozone reaction known in atmospheric chemistry was also relevant for indoor areas. Singer et al.[24] have measured relevant concentrations of formaldehyde after the application of cleaning products and air fresheners in the presence of ozone. Formaldehyde is also produced by combustion processes and heating of foods. Salthammer et al.[14] summarized the relevant indoor sources of formaldehyde in their recent publication.

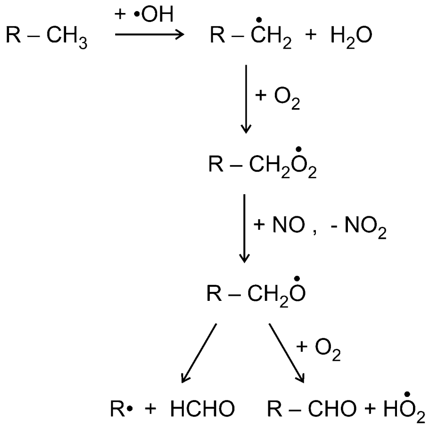
3.2. *Outdoor Sources*

The tropospheric photochemical processes that lead to the formation of formaldehyde are well-documented. Ozonolysis of alkenes, for example, following the mechanism described by Criegee[25] (Scheme 3), and the reaction mechanisms of alkanes and alkenes with hydroxyl radicals and nitric oxide (Scheme 4 and Scheme 5) were described in detail by Pitts and Finlayson[26] and Wagner and Zellner.[27]

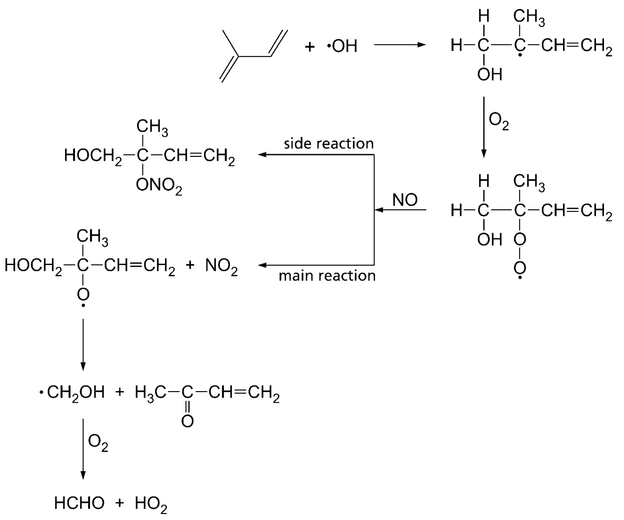


Scheme 3. Formation of carbonyl compounds from the alkene/ozone reaction.[25] 1) Primary step to form the ozonide, 2) and 3) decomposition pathways leading to carbonyl compounds.

The rate of the alkane–OH reaction depends on the temperature and increases with increasing length of the alkyl chain.[10] The half-life of methane in the presence of OH is about five years. Under ambient conditions, the HCHO path is usually slower than formation of HO_2 and higher aldehydes (Scheme 4). When being formed, formaldehyde is rapidly photolyzed under production of intermediates like HO_2.[10]



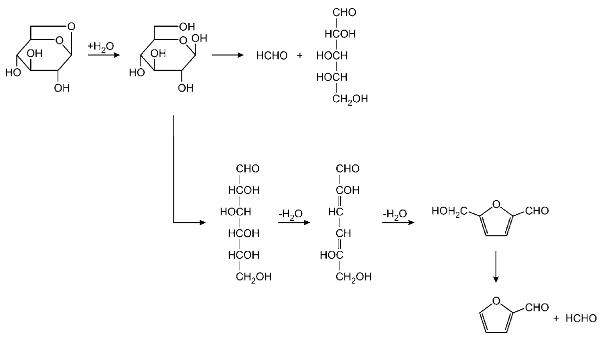
Scheme 4. Formation of formaldehyde from the atmospheric alkane/OH/NO reaction.[26,27]



Scheme 5. Formation of formaldehyde from the atmospheric isoprene/OH/NO reaction.[26,27]

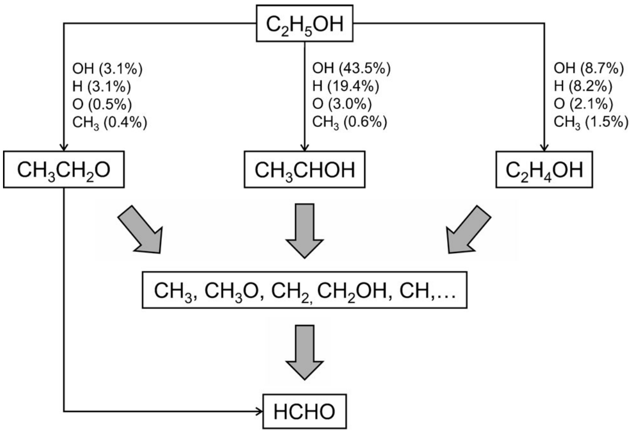
The thermal decomposition of cellulose also forms a number of carbonyl compounds, including formaldehyde. The causes of this are mostly uncontrolled processes such as forest fires[28] and the controlled burning of wood in household wood-burning heating ovens.[29] Shen and Gu[30] postulate a mechanism by which furfural and formaldehyde are formed from degradation of the cellulose unit via levoglucosan. The two major pathways of the levoglucosan reaction are shown in Scheme 6.

Intensive discussions are currently taking place concerning the sustainability of biofuels such as ethanol, higher alcohols, dimethyl esters, and long-chain methyl esters. As these compounds already contain oxygen in their molecular framework, there are significant differences to the combustion chemistry of conventional hydrocarbons. Kohse-Höinghaus et al.[12] reported on the reaction paths in the conbustion of different biofuels. The authors conclude that such processes can generally be expected to produce carbonyl compounds, particularly formaldehyde. Leplat et al.[31] come to similar conclusions following their research on the combustion



Scheme 6. Postulated mechanism for the formation of formaldehyde from levoglucosan during the combustion of cellulose.[30]

chemistry of ethanol under varying conditions. In the first step of ethanol decomposition, hydrogen abstraction by OH and H is the driving force, which primarily leads to CH_3CH_2O, CH_3CHOH, and C_2H_4OH (Scheme 7). Formaldehyde is then directly formed from the ethoxy radical[32] when it splits off a methyl radical and from secondary intermediates like CH, CH_2, CH_3, CH_3O, and CH_2OH. Detailed reaction schemes are provided by Leplat et al.[31]



Scheme 7. Simplified scheme for the formation of formaldehyde from the combustion of ethanol.[31]

4. Formaldehyde in Ambient Air

4.1. Outdoor Air

The number of publications on formaldehyde in the indoor and outdoor air is quite considerable. Table 1 and Table 2 show a cross section of data which represents both the different areas of concentration ranges and regional locations. Data was taken both from the usual databases and previous research.[7,11a,14,33] Conventional atmospheric chemistry long considered formaldehyde as one of many target compounds in the complex reaction schemata of atmospheric components. It is an important source of the OH radical, which is the major detergent of the atmosphere,[10] and therefore contributes to the formation of secondary organic aerosols and interacts with other dissolved species in clouds.[34] Formaldehyde can be found as an atmospheric trace element in outlying areas and is thus to be considered as ubiquitous.[35]

The formaldehyde concentrations in urban regions differ greatly. In northern and central Europe and in the United States, average values between 5 and 15 ppb are typical. The sometimes very high concentrations in Asian and South American megacities have different causes. The intensive solar irradiation[36] combined with high concentrations of reactive organic compounds such as alkenes leads to photosmog causing a large proportion of the formaldehyde formation in metropolitan areas like Beijing, particularly in the summer months.[37] Today, cities with high photochemical air pollution typically have an average formaldehyde concentration of between 20 ppb and 30 ppb with peaks of 40 ppb to 50 ppb. Most studies attribute secondary VOC reactions for the major contribution to atmospheric formaldehyde.[13,38,68] However, highly polluted urban air is not necessarily correlated to high formaldehyde concentrations as shown by Elshorbany et al. for the city of Santiago de Chile.[45]

The highest formaldehyde values have been recorded in Rio de Janeiro for some years. Corrêa et al.[11c,39] measured a considerable increase in the formaldehyde concentration between 1998 and 2004, which they attributed to the increasing use of biofuels. Improved engine technologies then led to a gradual decline in the concentrations (Figure 1). Gaffney and Marley[40] also closely investigated the increasing significance of formaldehyde as an outdoor air pollutant resulting from fuel emissions.

4.2. Indoor Air

Formaldehyde has been the most important substance subject to indoor air research for decades. Beginning with the often very high indoor concentrations in the 1960s and 1970s, largely caused by the hydrolysis of urea–formaldehyde resins, great efforts were made to significantly reduce the release of formaldehyde into indoor air.

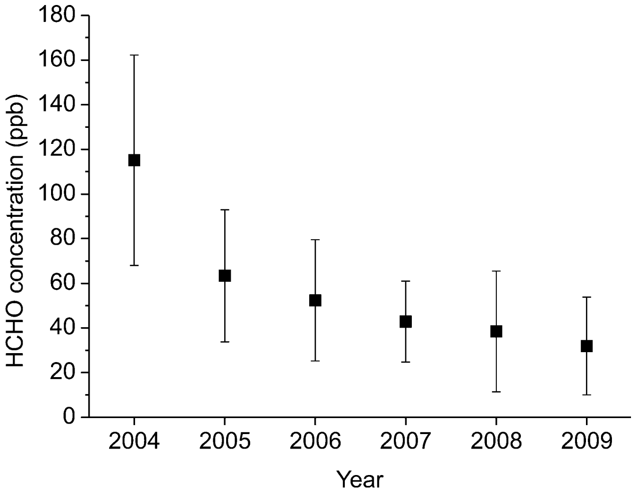


Figure 1. Formaldehyde concentrations (mean values, minima, maxima) in Rio de Janeiro. The data were taken from Corrêa et al.[39b]

Table 1: Formaldehyde concentrations in outdoor air as determined in different international studies (GM = geometric mean). For better comparison mass-related data were converted to ppb and are labeled with the footnote [a].

Location (outdoor air)	C_{HCHO} [ppb]		Comments	Ref.
rural European sites	0.4–5.5	range	1993–1996	[35b]
Central Amazonia	0.5–3	range	1998	[35a]
Riverside, California	1.7–11.2	range	2003, during wildfire activity	[28]
Nagoya, Japan	4.7[a]	GM	1998, Feb.	[41]
Beijing, China	16.9–49.0[a]	range	2006, during haze days	[33d, 37]
	26.82	average		
Shanghai, China	9.9–40.4[a]	range	2007, Mar. during high-air-pollution days	[33b]
	24.0[a]	mean	2007, Oct.	
	2.7–13.7[a]	range		
	5.6[a]	mean		
Kaohsiung City, Taiwan	5.9–31.9[a]	range	2006, May–Dec.	[42]
	15.2[a]	average		
Ansan, South Korea	2.2–42.2	range	2004–2005	[43]
	20.6	median		
Mexico City, Mexico	12.7–23.9	averages	2003, monthly (low: Oct.; high: Feb.)	[44]
	21.8–38.8	maxima	2003, monthly (low: Oct.; high: Apr.)	
Mexico City, Mexico	3–27	range	2003, Apr.–May, metropolitan area	[13]
Rio de Janeiro, Brazil[b]	1.52–5.07	averages	1998, daily averages Feb.–June	[11c]
	21.97–112.6	averages	2001, daily averages Feb.–June	
Santiago de Chile	2–7	range	2005, Mar.	[45]
Izmir, Turkey	1.0–30.1[a]	Range	2003–2004, May–May	[46]
	5.9[a]	average		
Cairo, Egypt	33	mean	1999, average of spring and summer values	[11b]
Beirut, Lebanon	0.6–12.2	range	2003, July–Sep.	[47]
	3.9	median		
Kuopio, Finland	35/55	maximum	1998, maxima in May/July during daytime	[48]
	1.0–2.2	background	1998, during nighttime	
Uppsala, Sweden	1.1[a]	GM	1998, Feb.–May	[41]
Milan, Italy	1.5–13	range	2002, July–Aug.	[49]
Rome, Italy	1.0–5.7[a]	range	time period unknown	[50]
	2.0[a]	median		
Athens, Greece	0.04–31.6[a]	range	2000, June–Dec.	[51]
	12.9[a]	median		
Southern California	5.0–6.1	range	1988–1989, Sep.–Sep., Anaheim. Azusa, Burbank, Hawthorne, Upland, Los Angeles	[52]
	20.7–29.4	maximum		
Los Angeles, USA	40	average	1961, Sep.–Nov.	[53]
	150	maximum		
USA	5.2[a]	median	1999–2001, RIOPA Study	[54]

[a] Converted to ppb. [b] See Figure 1 for 2004–2009 data.

The Federal Environment Agency has since measured a significant drop in the average level of formaldehyde pollution in German households between 1985/86 and 2003/06 in, for example, its Environment Survey.[14] The RIOPA study[54] comes to similar conclusions for the United States. Taking into account further data (see Table 2), formaldehyde concentrations significantly under 40 ppb can be expected in normal living conditions in Central European and North American households. Higher concentrations can sometimes be measured in Asian and South American households. It should, however, be mentioned that the studies are not fully comparable because detailed information on room climate, measurement conditions (samples taken over shorter or longer periods), and the influence of ventilation (air exchange, artificial or natural ventilation) are in many cases not available. High concentrations of formaldehyde continue to occur in certain special environments. These include temples,[66] medical laboratories,[21] and museums.[20] Although building products continue to be the largest indoor source of formaldehyde emissions, chemical reactions resulting from the increasing use of terpenoid compounds and rising ozone levels in the troposphere are gaining more and more significance.[69] The growing application of unvented space heaters also provides a new source of formaldehyde and other gaseous polutants in the indoor environment.[70]

5. Evaluation of Indoor and Outdoor Concentrations

The trends in formaldehyde concentrations in the indoor and outdoor air require a change of paradigm. In our urban environment, average formaldehyde concentrations up to 40 ppb indoors and 15 ppb outdoors can be considered as

Table 2: Formaldehyde concentrations in indoor air as determined in different international studies (GM = geometric mean). For better comparison mass-related data were converted to ppb and are labeled with the footnote [a].

Location (indoor air)	C_{HCHO} [ppb]		Comments	Ref.
Germany	60.0[a]	maximum	2003–2006, survey for children	[55]
	19.2[a]	median		
United States	16.4[a]	median	1999–2001, RIOPA Study	[54]
Rome, Italy	10.5[a]	median	time period unknown, kitchen	[50]
Strasbourg, France	4.9–75.8[a]	range	2004–2005	[56]
	21.8[a]	redian		
Paris, France	28.0[a]	GM	2001, Mar.–June	[57]
Southern Finland	9.0[a]	mean	2001–2006	[58]
Uppsala, Sweden	6.8[a]	GM	1998, Feb.–May	[41]
Nagoya, Japan	14.3[a]	GM	1998, Feb.	[41]
Shimizu, Japan	15.2[a]	GM	2000, summer	[59]
	10.1[a]	GM	2001, winter	
Hangzhou, China	10.0–200.2[a]	range	2006, Mar.–Apr., public places	[60]
Mexico City, Mexico	3–99[a]	range	time period unknown, different locations	[61]
Quebec, Canada	7.8–73.3[a]	range	2005, Jan.–Apr.	[62]
	18.7–39.4[a]	GM		
Ankara, Turkey	1.9–706	range	2004, Apr.–May	[63][63]
	54.7[a]	GM		
Cairo, Egypt	78.7[a]	average	1999, average of spring and summer values	[11b]
Dhaka, Bangladesh	21.4[a]	GM	2005–2006, Dec.–Jan., biomass burning	[64]
	30.1[a]	GM	2005–2006, Dec.–Jan., fossil burning	
	53.7[a]	GM	2005–2006, Dec.–Jan., gas burning	
Hongkong	69.8[a]	median	2002, Nov.	[65]
Hongkong	89.7–122.2[a]	average	2005, temples, non-peak period	[66]
	171.2–317.9[a]	average	2005, temples, peak period	
Chuoku, Japan	230–1030	range	2004, anatomy laboratory	[21]
Hannover, Germany	16–89.6[a]	range	2003–2004, museum storage rooms	[20]
Louisiana, Mississippi, USA	3–590	range	2007–2008, Dec.–Feb., mobile homes	[67]
	77	GM		

normal. "Normal" is, however, not to be confused with "safe" or "acceptable". It should simply be noted that, under current environmental policies, formaldehyde as an air pollutant is a consequence of our society and the need to supply food, clothing, housing, and mobility to currently 7 billion human beings. Air pollution control strategies and modern technologies already helped to lower formaldehyde concentrations in highly polluted areas like Los Angeles[52,53] (see Table 1) and Rio de Janeiro[11c,39] (see Figure 1). On the other hand, the increasing use of biofuels combined with the continuously increasing traffic density provides a potential source of formaldehyde, acetaldehyde, and saturated and unsaturated hydrocarbons.[12,40]

In the data collected in Table 2, the range 40 ppb to 80 ppb was defined as "elevated" for indoor air and anything above 80 ppb indoors as "polluted" taking into account the WHO guideline of 80 ppb[9] (see Figure 2). As there is no similar guideline value for outdoor air, concentrations over 15 ppb were evaluated as "elevated". It can be seen from Figure 2 that compliancy with very low guideline values, regardless of whether they are toxicologically founded, is practically unachievable because outdoor concentrations of 8 ppb are often exceeded.

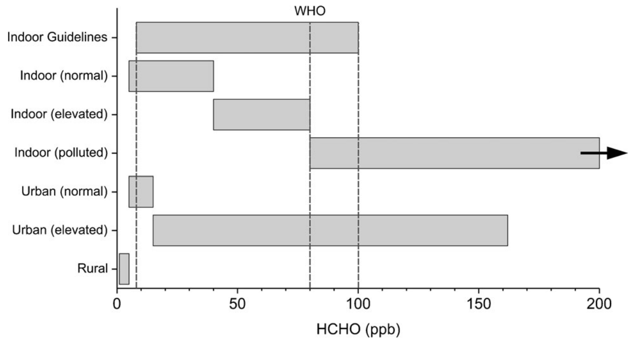


Figure 2. Range of formaldehyde concentrations in indoor and outdoor air. The range of current indoor guideline values[7] between 8 ppb and 100 ppb is also provided.

Some studies have examined the relationship between indoor and outdoor air. Liu et al.[54] compared indoor and outdoor air concentrations in the RIOPA study using 353 measurement results. The median of the data is significantly above the 1:1 line, which indicates a much stronger influence of the indoor air in this sample test. Santarsiero and Fuselli[50] come to similar conclusions on the basis of an analysis of the main components for their data collected in Rome. In metropolitan areas with serious air pollution, such as Beijing, indoor/outdoor ratios of 1.62–6.37 were measured for the summer months and 2.05–10.99 for the winter months.[33a] In clean-room environments such as hospitals, the outdoor air concentrations are now often higher (0.11–21.3).[71] I/O ratios of 1.4–4.4 were measured for Mexico City and Xalapa by Baez et al.[61] Regardless of the substance formaldehyde, the I/O ratio for an air pollutant always involves the question of correct ventilation. Extremely high concentrations of particles and many chemical compounds are detectable in the outdoor air.[72] In many cases, an exchange of outdoor and indoor air is therefore only possible with appropriate filter systems. In Europe, artificial ventilation systems are not yet preferred, but they are coming into use more and more often.

6. Summary

In the urban environment, people inhale indoor air most of their time. Usually, measured I/O ratios are greater than 1. This means that on average, indoor formaldehyde levels are still higher than outdoor levels. Therefore, formaldehyde has not yet moved from being an indoor pollutant to being an outdoor pollutant. The differences in indoor and outdoor concentration levels are, however, becoming smaller and in several cases an overlap can already be observed (Figure 2). The main processes involved in forming formaldehyde are again summarized in Figure 3. While authorities, research institutes, and industry are making great efforts to develop lower-emission building materials, massive industrial expansion, increasing energy consumption, and the desire for more mobility are having a range of negative consequences on the air quality. For example, the combustion-related problems of alternative fuels will have to be solved very soon for the world's stock of over a billion motor vehicles.[12,40] More research is also needed on how homes can be effectively ventilated in high-pollution areas, not only in terms of the energy involved, but also with regard to health aspects.[73]

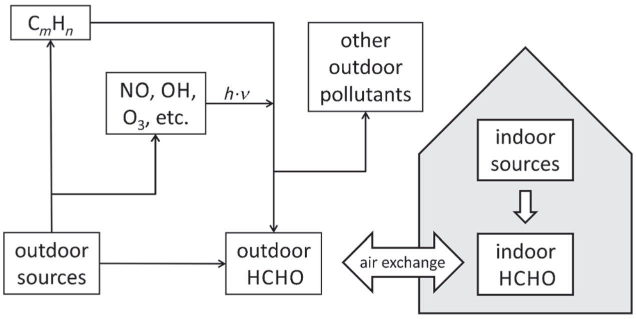


Figure 3. Overview of the major processes for formaldehyde formation and indoor/outdoor relationship by air exchange.

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