Indoor and outdoor aldehyde concentrations in a medium-sized French town

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Abstract

Aldehydes are air pollutants with the potential to act as strong sensory irritants. Outdoors, these compounds play a part in the complex system of photochemical atmospheric reactions, and they are directly released by traffic and other combustion sources. Indoors, numerous emission sources have been identified, for example tobacco smoking or furniture.

The objective of the present study was to measure average concentrations of selected aldehydes in typical urban environments.

A pilot study was carried out in Nancy, a medium-sized town in the Northeast of France. Outdoor concentrations of seven aldehydes were measured by exposing passive samplers for two periods each lasting five days. 30 samplers were installed at background sites and at sites where people spend more of their time. Moreover, 20 volunteers were equipped with personal samplers, which they carried on them during the first five days. Concentrations were also measured in their homes and offices.

The results show that the highest outdoor concentrations are found in the centre of Nancy. However, aldehyde concentrations are much higher indoors than outdoors, even when compared with a period of meteorological conditions "favouring" higher aldehyde concentrations. Office and home concentrations agree with concentrations obtained with personal samplers. It is furthermore shown that the sum of formaldehyde and acetaldehyde concentrations may be used as a tracer for the group of aldehydes studied.

Introduction

Aldehydes can be strong sensory irritants. Moreover, formaldehyde and acetaldehyde have been classified by the World Health Organisation as probably and potentially causing cancer [*1*], respectively.
Research is therefore stimulated in order to measure concentrations of these compounds in the ambient air, and to estimate the chronic exposure to these compounds.
Outdoors, aldehydes play an important role in the complex system of photochemical atmospheric reactions [*2*], and they are directly released by traffic and other combustion sources [*3, 4*]. Indoors, personal activities (tobacco smoking or cooking) as well as material emissions (for example from furniture) result in increased concentrations [*5*]. It was furthermore suggested that aldehydes might additionally be formed indoors by reactions between volatile organic compounds and atmospheric oxidants [*6*].
The first objective of the present study was to examine different urban living environments with respect to their contribution to personal aldehyde exposure. For this reason, concentrations of a number of aldehydes, averaged over several days, were obtained at numerous sites (indoors and outdoors) and with portable samplers carried by volunteers. A comparison of these results will reveal which environments may be more important with regard to personal exposure.
It was also the aim of this study to find methods that may help to reduce the large amount of information that is typically available when characterising many sampling sites and numerous compounds.

Experimental

Analytical

Passive sampling devices (Radiello, Fondazione Salvatore Maugeri, Padova, Italy [*7*]) equipped with dinitrophenyl hydrazine (DNPH) sampling cartridges and ozone scrubbers [*8*], were used to quantify concentrations of the compounds listed in Table 1.
Passive samplers provide average concentrations of the selected exposure time.
After exposure, the sampling cartridges were extracted with 2 ml acetronitrile. The extracts were analysed with HPLC separation (KROMASIL C18 150 mm-3mm - 3.5 μm) and UV detection (λ=365 nm). Compounds were identified by their individual retention times. The analytical results were corrected for blanks using six non-exposed field blank sampling tubes. However, this was only necessary for formaldehyde.
The sampling speed of passive samplers should be limited by the diffusive transport of molecules into the sampler. The sampling speed is usually expressed as an uptake rate in (ml/min) and depends on compound properties like the molecular mass. The sampler manufacturer provided aldehyde uptake rates for

formaldehyde, acetaldehyde and acroleine. Additional uptake rates were experimentally determined for the following aldehydes: butanal, pentanal, hexanal, heptanal, octanal, nonanal, furfural and benzaldehyde. For this reason, the samplers were exposed to a defined and controlled aldehyde test atmosphere in an emission test chamber for approximately 3.5 days [*9*]. No correlation was observed between the experimentally determined uptake rates (not presented in this paper) and theoretical values based on compound-specific diffusion coefficients in air, backing up previously published observations [*10*]. This point requires further clarification, and complementary studies are underway.

Sampling protocol

The measurement campaign was carried out in Nancy, a medium-sized town (ca. 100 000 inhabitants) in the Northeast of France, in September 2000. It consisted of two parts each lasting five days. The weather conditions of the first part were characterised by rain episodes and light winds coming from various directions. During this part, 22 samplers were exposed at outdoor background sampling sites, which had been selected to cover the whole area of Nancy. In addition, samplers were installed at 8 sites where people spend more of their time (a square in front of the central station, a pedestrian zone, a small street with restaurants, etc.). All samplers were installed about 3m above ground and sheltered by aluminium boxes.
During these first five days, 20 volunteers carried a personal sampler on them (within breathing zone). Half of them worked indoors (offices) and the other half outdoors (gardeners). All participants installed samplers indoors in their sleeping rooms and in their offices.
After this first part, the campaign lasted for another five days, where 10 samplers were installed outdoors. This time, the weather was dry and rather sunny.

Repeatability of the sampling procedure was tested by exposing pairs of samplers simultaneously at four different outdoor sampling sites. When plotting the total amounts of all quantifiable compounds in one sampler over the total amounts found in the second sampler, a correlation coefficient of 0.89 ($p<0.0001$) was obtained.

Results and Discussion

Concentrations

Table 1 presents the concentrations obtained at different environments and with the samplers carried by volunteers (median and maximum concentrations in $\mu g/m^3$ for all compounds and environments).
Butanal and nonanal could not be quantified, due to the co-elution of compounds sampled together with the target molecules. Furthermore, furfural was never detected in the samples. These compounds are therefore not included in Table 1.

Two samples contained acroleine and croton aldehyde, whereas benzaldehyde was present in 12 samples.

Table 1: Median and maximum concentrations of different environments, time periods and activities

	Outdoors: background sites part I		**Outdoors: Frequently visited sites part I**		**Outdoors: Part II**	
Compound	median (µg/m³)	maximum (µg/m³)	median (µg/m³)	maximum (µg/m³)	median (µg/m³)	maximum (µg/m³)
formaldehyde	1.19	1.91	1.91	2.55	6.09	11.17
acetaldehyde	2.84	3.73	3.60	8.65	5.76	8.74
acroleine	0.00	0.00	0.00	0.00	0.00	2.11
benzaldehyde	0.00	0.00	0.00	0.09	0.00	0.00
pentanal	0.64	2.04	0.42	2.11	0.84	2.50
hexanal	0.74	1.59	0.77	1.20	1.60	2.40
heptanal	2.63	7.92	2.45	9.47	3.76	13.89
octanal	2.07	5.15	2.12	5.99	3.12	9.58
	Indoors: sleeping rooms part I		**Indoors: offices part I**		**Samplers carried by participants part I**	
Compound	median (µg/m³)	maximum (µg/m³)	median (µg/m³)	maximum (µg/m³)	median (µg/m³)	maximum (µg/m³)
formaldehyde	14.34	127.26	14.33	24.16	13.53	38.04
acetaldehyde	22.84	85.56	16.35	24.26	23.27	68.04
acroleine	0.00	0.00	0.00	0.00	0.00	0.00
benzaldehyde	0.00	9.04	0.00	2.57	0.00	6.74
pentanal	4.04	16.77	2.26	8.26	3.07	12.46
hexanal	20.64	91.66	12.00	25.03	14.83	59.73
heptanal	12.00	33.43	8.41	10.89	10.49	25.96
octanal	9.85	28.87	6.75	9.97	9.56	24.44

Formaldehyde and acetaldehyde concentrations showed excellent agreement with those of a previous study carried out in Nancy [*11*], and good agreement with literature values was observed for the other compounds (for example [*3, 10, 12*].

The samplers carried by the participants should give a true image of the average aldehyde concentrations to which the participants were exposed during the measurement campaign. A direct comparison of median values already reveals that personal sampler concentrations were much closer to those observed indoors than to outdoor concentrations. Evidently, indoor emission sources like furniture or personal activities (smoking) will play a very important role in terms of increased aldehyde concentrations.

Total Concentrations

We decided to simplify the subsequent discussion by introducing a sum parameter, hence reducing the large number of experimental results to a few, easily comparable data sets. In analogy with the total volatile organic compound (TVOC) concept suggested by the European Commission for the evaluation of indoor air quality [*13*], we added the individual concentrations c_i of all aldehydes from one sampler so as to obtain a sum parameter K_Σ (eqn (1)):

$$K_\Sigma = \sum_{i=1}^{n} c_i \qquad (1)$$

K_Σ may be considered as a concentration [$\mu g/m^3$]. Note that K_Σ does not directly follow the original definition of TVOC.

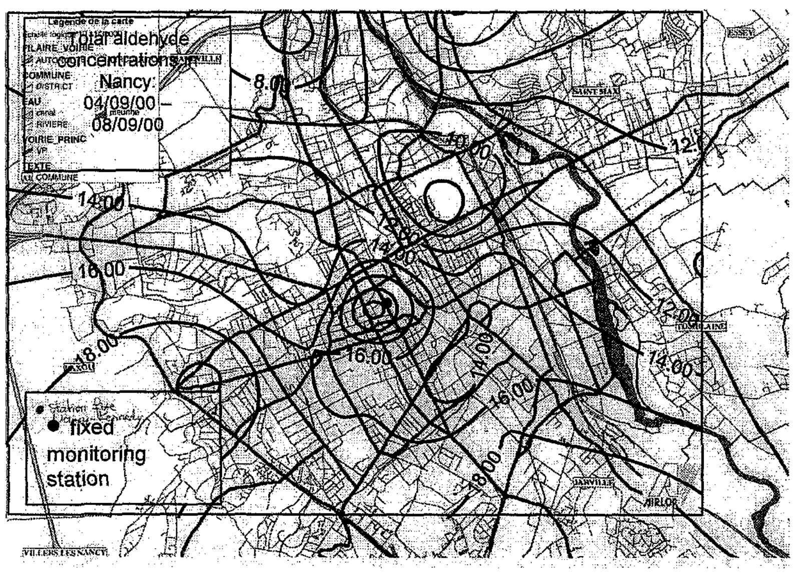

Figure 1: Isoconcentration plot of the sum of concentrations in Nancy, using a geostatistical interpolation procedure (kriging)

The outdoor sum parameter K_Σ of all background sites was taken to draw isoconcentration lines, using a geostatistical interpolation procedure (kriging). Figure 1 shows that the highest sum of aldehyde background concentrations during the first part of the study was found in the centre of Nancy, close to the fixed monitoring station. This is probably due to meteorological conditions and a local topography – Nancy is partially situated in a valley basin – hampering pollution dispersion, and to higher traffic volume in the town centre.

Several data sets characterising different environments (outdoors, offices, sleeping rooms), time intervals (first and second part of the measurement campaign) and activities (working indoors and outdoors) are available. Most of these data sets showed a non-Gaussian distribution and were therefore compared by means of a non-parametric Rank Sum test. Table 2 presents the probabilities p, where $p<0.05$ suggests a significant difference between two data sets. The comparison is based on the sum parameters K_Σ.

Table 2: Comparison of data sets using a rank sum test

Data sets	p
Outdoor background sites part I / Outdoors Part II	<0.001
Indoors (sleeping rooms and offices) part I / Outdoor background sites part I	<0.001
Indoors (sleeping rooms and offices) part I / Outdoors Part II	<0.001
Samplers carried by participants part I / Outdoor background sites part I	<0.001
Samplers carried by participants part I / Indoors (sleeping rooms and offices) part I	0.474
Samplers carried by participants working indoors / Samplers carried by participants working outdoors	0.354

The following observations can be made when comparing the different data sets:

- Rather rainy weather during the first part of the study led to low aldehyde concentrations, which is due to an abatement of these water-soluble compounds. Dry and rather sunny weather resulted in significantly higher outdoor concentrations.
- However, indoor concentrations (sleeping rooms and offices) are much higher than outdoor concentrations, even when using results originating from the second part of the study. This may be explained by the presence of numerous indoor emission sources, and the fact that indoor ventilation is often poor.
- Concentrations obtained from personal samplers show a significant difference from those outdoors. The difference is not significant when compared to indoor concentrations.

- Interestingly, and in contrast to what would be expected, the difference in concentration obtained with the personal samplers carried by volunteers working indoors and those working outdoors does not seem to be significant. It may be speculated that the volunteers working outdoors, i.e. garden staff, spend some time in the proximity of outdoor emission sources like lawnmowers etc. It should be kept in mind, though, that only small sampling groups are compared.

Tracer Compounds

Another possibility to reduce the high amount of data is to identify one or a few tracers, which may then be used to indicate the concentrations of all aldehydes. Several of the studied compounds were tested as potential tracer compounds. The best results were obtained when taking the sum of formaldehyde and acetaldehyde concentrations, as is depicted in Figure 2.

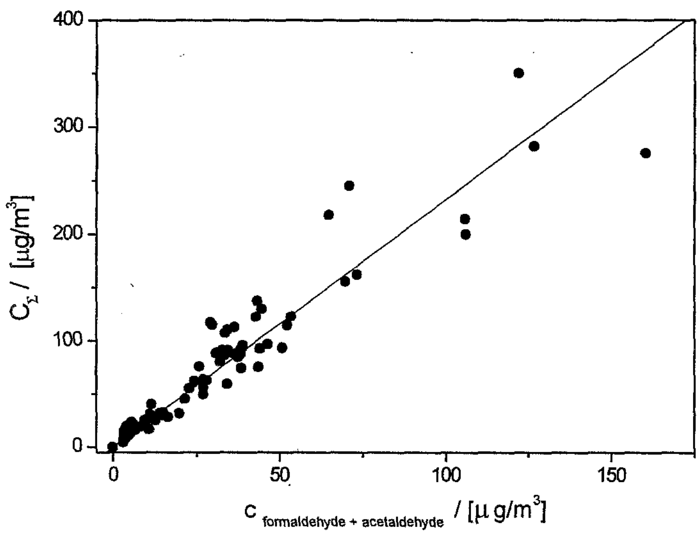

Figure 2: The sum of all aldehyde concentrations of all samplers plotted over the sum of formaldehyde and acetaldehyde concentrations

When plotting the total concentrations K_Σ over the sum of concentrations of formaldehyde and acetaldehyde for all analysed samples, a good linear correlation with a correlation coefficient $r=0.95$ is observed:

$$K_{\Sigma} = 2.32 \times c_{formaldehyde+acetaldehyde} \quad (2)$$

Formaldehyde and acetaldehyde may be used together as tracers for the group of compounds studied. This result is important from a practical point of view, since these two compounds can be easily analysed.

Conclusions

This pilot study provides results that are in good agreement with existing literature data.

Higher indoor aldehyde concentrations and the fact that people spend up to 90% of their time indoors [*14*] lead to the conclusion that indoor environments will in many cases be much more important in terms of a chronic aldehyde exposure than outdoor environments.

By using the sum of measured aldehyde concentrations (in analogy with the TVOC concept), the discussion of large data sets, as are typically obtained when characterising many different environments and compounds, was considerably simplified. A further simplification consists in using the sum of formaldehyde and acetaldehyde concentrations, which are tracer compounds for the group of aldehydes studied.

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