Gas phase determination of aldehydes in three sites of Mexico City

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Abstract

Aldehydes, were analyzed in air samples at four places in the Valley of Mexico basin. These were, one urban, one suburban and two rural places, one of them within the area of influence of Mexico City and the other upwind and taken as the reference site.

1 Introduction

Mexico City is a most interesting case for the study of air pollution. Within its metropolitan zone live 20 million people (20.4% of the national population). High mountains up to 1000 meters above downtown level run from the northwest to the southeast along the western side of the urban area. Many efforts have been made to reduce air pollution levels with some success on lead, carbon monoxide and extreme ozone peaks. An extensive air quality monitoring network has been in operation since 1986. this has been enlarged, updated and fitted with an array of monitors. However, there exists a wealth of pollutants of great importance for the understanding of the air pollution phenomena not usually monitored for this kind of networks. Among the organic compounds, aldehydes are an important class.

Aldehydes are key species in the chemistry of tropospheric ozone and photochemical smog. These are emitted as primary pollutants from internal combustion engines. The use of additives such as MTBE or use of ethanol fuels may increase these emissions. Aldehydes are also formed in the atmosphere as secondary products on the photo-oxidation path of hydrocarbons, both natural or anthropogenic. For their reactivity toward hydroperoxy and hydroxy radicals, and the ability to undergo direct photolysis, C1-C3 aldehydes are the most relevant. Formaldehyde has been measured in air by different techniques; The use of 2,4 dinitro-phenylhydrazine (DNPH) and HPLC enables to analyze a series of
aldehydes in the same experiment. Derivatization with DNPH has been used in impingers, filters, and denuders.

2 Experimental

Sampling was made from January 24 to March 14 of 1996. Four sites were chosen within the Valley of Mexico Basin: University Campus, El Ajusco, El Desierto de los Leones. University Campus is southern part of Mexico City (Table 1). Samplers were placed on the roof of the Center for Atmospheric Sciences on the east side of campus that is 700 hectares. Dominant tree species are conifers and eucalipt. The site on El Ajusco on the southern outskirt of the city and 1000 meters above downtown level. Samplers were on the roof of a one storey building in a conservation area in regeneration process after being severely deforested. Dominant tree species is Quercus. The nearest neighborhood and roads are 2 km away. Samplers on El Desierto de los Leones were on the roof of a colonial monastery to the west of the city, on the mountain leaving the Valley. The monastery is in a perturbed forest of Abies and Pinus, 800 meters above downtown level. The fourth place was a control place. It was in a clear in an Abies forest in good conservation state in the mountain that makes the northern border of the Basin and overlooking the city of Pachuca.

<table>
<thead>
<tr>
<th>SITE</th>
<th>CODE</th>
<th>DATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>University Campus in Mexico City</td>
<td>UC1</td>
<td>Feb 12-16</td>
</tr>
<tr>
<td></td>
<td>UC2</td>
<td>March 4-8</td>
</tr>
<tr>
<td></td>
<td>UC3</td>
<td>March 11-14</td>
</tr>
<tr>
<td>El Ajusco</td>
<td>A1</td>
<td>Feb 7-10</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>Feb 20-23</td>
</tr>
<tr>
<td>El Chico</td>
<td>C</td>
<td>Jan 24-26</td>
</tr>
<tr>
<td>El Desierto de los Leones</td>
<td>DL</td>
<td>Jan 31-Feb 3</td>
</tr>
</tbody>
</table>

Table 1: Sampling sites

Sampling was made in concentric denuders of 242 mm length and three channels with a gap of 3mm each for the air flow (URG 116s, Merrit Mill Road, Chapel Hill, NC. USA). The denuders were impregnated with a 1% of DNPH in a 1.5% dilution of H₃PO₄ for the aldehydes. Air flow was 10 l/min. Samples were collected in two periods of six hours from 7:00 a.m. to 7:00 p.m. and a third
period of 12 hours from 7:00 p.m. to seven a.m.. To prepare the denuders 0.5 ml of the solutions were introduced into the concentric gaps then the denuders were rotated to wet all the contact area. The surface was dried by a zero air flow of 2 l/min. The denuders were closed with its caps and sealed with Teflon film. After sampling, the reactive film for aldehydes was removed by rising with two 10 ml portions of acetonitrile. The solutions were kept under refrigeration until analysis at the end of the sampling period.

Aldehydes were analyzed by HPLC, 20 μl of the sample solution were injected to a Perkin Elmer liquid chromatograph. The column was a Spherisorb %S reverse phase, 15 cm long and 46 mm on diameter, with a flow of 1 ml/min of a mobil phase 55% acetonitrile and 45% water. Detection was made with an UV/Vis Perkin Elmer LC 1200 detector fixed at 360 nm.

3 Results and discussion

3.1 Formaldehyde

Among the aldehydes, formaldehyde is the specie that shows the highest population mean (23.35 ppb). This is 66.7 % higher than that for acetaldehyde, 84.4% higher that benzaldehyde 83.9% higher than butyraldehyde, and 94.2 % higher than propionaldehyde. The sampling period with the highest concentration was UC1 (Table 1) with a sample mean of 58 ppb. This mean is 33.5 % higher than the following (UC2) and 46.7% higher than the next (UC3), both from

![Formaldehyde](image-url)
University Campus a month later. The place with the second higher sample mean of 13.1 ppb was El Ajusco, at the beginning of February and 9.8 ppb two weeks later. This site has the stronger urban influence being nearer to the city and downwind the dominant air flow on the surface. The third place is El Desierto de los Leones (DL) showing a weaker urban influence showed a sample mean of 12.2 ppb on the first days of February. The site showing the highest hourly mean was University Campus (UC1) at night with 79.1 ppb, it follows the morning sampling period with 57.4 ppb and then the afternoon with 37.7 ppb on the same dates.

In this work the highest concentration was 97.8 ppb in UC1 at night. A previous study on atmospheric formaldehyde in Mexico City by Baez et al using DNPH impregnated cartridges reports a maximum concentration of 110.4 ppb in the morning, however they did not take any sample at night. University Campus is the only place that shows higher levels of formaldehyde at night. This fact may be explained by formation due to night time oxidation of hydrocarbons. Another contribution may be switching off direct photolysis, leaving oxidation by hydroxyl and hydperoxy radicals the only sink paths acting at night. Concentration levels on the control site were.

Concentrations on the rural site upwind of Mexico City (Cl) showed a sample mean of 1 ppb with the highest value of 1.4 ppb on the morning. In comparison Trapp obtained 1.7 ppb in a rural site in Venezuela.

3.2 Acetaldehyde

![Acetaldehyde](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>Morning</th>
<th>Afternoon</th>
<th>Night</th>
</tr>
</thead>
<tbody>
<tr>
<td>DL</td>
<td>9.1</td>
<td>8.9</td>
<td>5.3</td>
</tr>
<tr>
<td>A1</td>
<td>9.1</td>
<td>9.9</td>
<td>5.1</td>
</tr>
<tr>
<td>A2</td>
<td>7.1</td>
<td>7.6</td>
<td>4.6</td>
</tr>
<tr>
<td>UC1</td>
<td>9.7</td>
<td>11.5</td>
<td>6.6</td>
</tr>
<tr>
<td>UC2</td>
<td>14.6</td>
<td>14.8</td>
<td>8.3</td>
</tr>
<tr>
<td>UC3</td>
<td>8.3</td>
<td>14.1</td>
<td>6.8</td>
</tr>
<tr>
<td>C</td>
<td>1.0</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 2: Acetaldehyde at different sites and sampling periods
Acetaldehyde’s concentration showed the second highest population mean of 8 ppb. The site with the highest sample mean was UC2 with 14.8 ppb in the afternoon, followed by UC3 and UC1, also in the afternoon. The daily trend observed in University Campus is to show small to moderate increases from the morning values and then a drop about the half for the night period. The suburban place, El Ajusco did show similar behavior but with a smaller increase in the afternoon and a significant drop at night. The two rural places showed a small decrease in the afternoon and a drop of about 50% at night although in the control site the concentration levels are one order of magnitude lower. However, the site DL still shows a considerable influence from the city.

In University Campus concentrations about 2%, 20% and 70% higher in the afternoon than in the morning are observed. In El Ajusco and Desierto de los Leones not so smaller concentrations were observed in comparison with the urban site, also small increases or reductions were observed in the afternoon in these two places. All suggest the air borne nature of acetaldehyde, and the balance between reacting sources and sinks. In average, concentrations at night are about 50% smaller that in the afternoon, night time chemistry, forming and consuming acetaldehyde, may be responsible for the more uniform concentration levels among urban and suburban sites.

3.3 Benzaldehyde

The population mean of all samples of benzaldehyde was 3.7 ppb, is the third
highest after acetaldehyde. University Campus shows the highest levels in all sampling periods. UC1 shows a sample mean of 8.2 ppb, UC2 one of 5.9 ppb and UC3 one of 8.6 ppb. In comparison, acetaldehyde was higher on UC2 and formaldehyde was higher on UC1. UC2 and UC3 show higher values in the morning followed by the afternoon, whereas UC1 shows higher level in the afternoon. The two sampling periods in El Ajusco, A1 and A2, show smaller sample means; 1.7 ppb and 1.2 ppb. Variations of concentration were also smaller on these sites. DL shows smaller concentrations. The control site shows even smaller concentrations. The daily trends in the urban site, increasing in the morning, decreasing in the afternoon and night. The lower levels in the suburban and rural sites downwind with small daily variations. The very low concentrations in the rural site upwind from the city. All these observations are related to the main source of benzaldehyde, tail pipe emissions and oxidation of benzene also emitted by cars. No other study reports benzaldehyde in Mexico City. Grosjean\textsuperscript{12} reports a maximum value of 0.6 ppb in Los Angeles Cal. at 8:00 - 9:00 a.m.

### 3.3 Propionaldehyde

In the control site propionaldehyde is not observed at all. The population mean of 1.4 ppb is the lowest of all aldehydes. The highest sample mean concentration of 3.8 were observed on A2. The highest hourly mean of 5.7 ppb was observed in the afternoon on A2. In A1 the afternoon also showed higher concentrations. In the urban place, UC1 reported higher hourly mean in the morning period, UC2 and UC3 showed higher levels in the afternoon. Grosjean\textsuperscript{13} reports 14.1 ppb on high

![Propionaldehyde](image.png)

Figure 4: Propionaldehyde at different sites and on different sampling periods
3.4 Butyraldehyde

The place showing the highest hourly mean of 9.1 ppb was A1 in the morning, in the afternoon the hourly mean was 8.8 ppb. But in A2, UC1 and UC2 levels were higher in the afternoon. UC3 showed higher concentration in the morning.

4 Conclusions

Some aldehydes were determined in the Valley of Mexico Basin. Higher levels of formaldehyde at night are evidence of an active night time chemistry. Accumulation of acetaldehyde, propionaldehyde and butyraldehyde in the afternoon was observed in the urban and downwind suburban sites, both on the south end of the city. This information could be useful on the analysis outputs from air quality models.
Acknowledgments

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Key words

Formaldehyde, aldehydes, denuders, Mexico City, night time chemistry

References


