

## The Formaldehyde and Acetaldehyde Content of Atmospheric Aerosol

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Received: June 6, 1994; November 2, 1994

O presente estudo refere-se às concentrações de formaldeído e acetaldeído associados a aerossóis atmosféricos. Os aldeídos em fase gasosa foram coletados utilizando microcolunas SEP PAK C18 impregnadas com solução ácida de 2,4-dinitrofenilidrazina (DNPH). Os aldeídos associados com os aerossóis atmosféricos foram coletados utilizando amostradores "high-vol" com filtros de fibra de vidro. Foram coletadas 16 amostras, em períodos de uma hora, em dois sítios de amostragem na cidade de Salvador, Bahia: uma estação de ônibus e um túnel. As concentrações máximas de formaldeído e acetaldeído na fase gasosa atingiram, respectivamente,  $109 \mu\text{g}/\text{m}^3$  e  $167 \mu\text{g}/\text{m}^3$ , enquanto as concentrações máximas desses compostos associados aos aerossóis atingiram, respectivamente,  $0,028 \mu\text{g}/\text{m}^3$  e  $0,055 \mu\text{g}/\text{m}^3$ . Mesmo esta pequena concentração na fase aerossol é muito maior que a estimada com base em um simples equilíbrio entre o aldeído dissolvido no filme aquoso associado ao aerossol, a concentração do aldeído em fase gasosa e as respectivas constantes de Henry.

The present work is concerned with the formaldehyde and acetaldehyde content of atmospheric aerosol. Atmospheric formaldehyde and acetaldehyde present in the gas-phase were collected using C-18 Sep Pak cartridges coated with an acidic solution of 2,4-dinitrophenylhydrazine (DNPH). Aldehydes associated with aerosols were collected on high-vol glass fiber filters. Sixteen source samples were collected during 1-hour periods in two sites located in the city of Salvador, Bahia: a bus station and a tunnel. The results obtained for formaldehyde and acetaldehyde attained values of  $109 \mu\text{g}/\text{m}^3$  and  $167 \mu\text{g}/\text{m}^3$  in the gas-phase, and  $0.028 \mu\text{g}/\text{m}^3$  and  $0.055 \mu\text{g}/\text{m}^3$  in the aerosol-phase, respectively. Even these small aerosol-phase concentrations are considerably higher than the equilibrium concentration values predicted from the water content of the aerosol, the simultaneously measured gas-phase concentrations, and the respective Henry's constants.

**Keywords:** formaldehyde, acetaldehyde, atmospheric aerosols

### Introduction

Aldehyde sources in the atmosphere include primary emissions from natural vegetation, industrial plants, incinerators and automobiles, as well as secondary ones via photo-oxidation of methane, isoprene, and other biogenic and anthropogenic hydrocarbons<sup>1</sup>. Concentrations of formaldehyde and acetaldehyde in the atmosphere are of great significance to atmospheric chemistry due to the strong influence these species have on photochemical reactions, which lead to the formation of important air pollution components such as nitric acid, peroxyacetyl nitrate (PAN), and several others<sup>1,2</sup>.

In the past decade a substantial amount of information on surface atmospheric levels of formaldehyde and acetal-

dehyde has been generated<sup>2-8</sup>. However, most of the knowledge about formaldehyde, and principally of acetaldehyde in the atmosphere comes from measurements of the gas phase. Because carbonyl compounds are polar they can easily interact with particles of condensed matter, be adsorbed on soot, or dissolved in rain and fog<sup>6</sup>. Therefore, until recently data concerning aldehyde levels in the aerosol phase were sketchy at best<sup>3,9</sup>. As such, information about aldehyde levels emitted in the gas- and aerosol-phase, and present in the two phases in the atmosphere, are needed for a more complete description of their atmospheric budgets.

The present work is concerned with efforts to determine aldehyde levels associated with atmospheric aerosols and their correlation with aldehyde concentration in the gas phase.

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## Experimental

### Site description

The metropolitan area of Salvador is located on the Atlantic coast of Brazil at 13°01'S and 38°31'W, with about 2 million inhabitants distributed over a 324 km<sup>2</sup> area. Salvador is a tropical city with average yearly maximum and minimum temperatures of 32 °C and 19 °C, respectively. The samples were collected in two sites:

- at a bus station which corresponds to an area of *ca.* 13,920 m<sup>2</sup>. The predominant traffic is diesel fueled buses which reach a rate of 150 buses/hour during the rush period. For four days, samples were collected hourly from 8 am to 9 pm. During the collection period the temperature varied between 27 °C and 30 °C; and

- at a tunnel which is 300 m long and contains four traffic lanes, two in each direction. It is representative of the vehicular pattern of the city of Salvador because the traffic includes light duty vehicles (average rate, 1980 vehicles/hour), which use both hydrous ethanol and gasohol (18-22% ethanol v/v in gasoline), and diesel-fueled heavy duty vehicles (average rate, 420 vehicles/hour). In 1992 the vehicular pattern of Salvador included 41.2% ethanol-fueled vehicles, 49.8% gasohol-fueled vehicles, 8.3% diesel-fueled vehicles, and 0.7% vehicles using other fuels. During the collection period the temperature varied between 29 °C and 31 °C.

### Reagent preparation

The DNPH solution was prepared by diluting 20 ml of concentrated DNPH solution (100 mg/ 100 mL, in a solution of 1% H<sub>3</sub>PO<sub>4</sub> in acetonitrile by volume) with 2.0 L of deionized water containing 1% H<sub>3</sub>PO<sub>4</sub>. The solution was then purified by three successive extractions with CCl<sub>4</sub>. The DNPH solution was stored in a 2.5 L glass bottle containing 200 mL of CCl<sub>4</sub> and a Teflon coated magnetic stirring bar. A more detailed account of the reagent preparation can be found elsewhere<sup>10</sup>.

## Sampling and Analytical Methods

### Aerosol phase

High volume samplers (Energética Ind. Com. Brazil) were employed to collect atmospheric aerosol on glass fiber filters (Energética Ind. Com. Brazil), at face velocities of *ca.* 28.9 m/min (*ca.* 1.13 m<sup>3</sup>/h). The filters were previously weighed, wrapped in aluminum foil and stored inside plastic bags under refrigeration. After sampling, the filters were weighed again and stored in the same way. Sections of 15.4 cm<sup>2</sup> from the 20.4 cm x 25.5 cm glass fiber filters were reacted with 5.0 mL of a 0.01% DNPH (1% phosphoric acid) aqueous solution for 20 min, under sonication. The liquid phase was then filtered and aliquots of 10 µL were injected directly into the HPLC system. The

detection limits of the method (S/N = 3, based on peak height) were around 159 pmol and 33 pmol for formaldehyde and acetaldehyde, respectively<sup>10</sup>.

### Gas phase

Formaldehyde and acetaldehyde were sampled at 1.0 L/min, for 1 hour, by two reverse-phase (C18) Sep-Pak micro columns (Waters Associates) connected in series; the micro columns were coated with DNPH, as described in detail elsewhere<sup>11</sup>. After sampling, the micro columns were eluted with 5 mL of acetonitrile and aliquots of 10 µL were injected directly into the HPLC system. The detection limits of the method (S/N = 3, based on peak height) were around 4.4 nmol and 2.4 nmol for formaldehyde and acetaldehyde, respectively. In all samples the aldehyde concentrations determined in the second micro columns were close to zero.

### Equipment and conditions

A Varian liquid chromatograph (model 2510) equipped with a Rheodyne injector (model 7125), with a 10 µL loop, and a variable UV/VIS detector (model 2550) was used. In order to obtain the lowest detection limit the wavelength and detector sensitivity were selected for formaldehyde and acetaldehyde, respectively at 350 nm (0.04 AUFS) and 365 nm (0.01 AUFS). The analytical column used was an Econosphere C18, 5 µm, 250 mm x 4.6 mm *i.d.* (Alltech). The mobile phase was acetonitrile: water (57:43 v/v) at 1.0 mL/min. A more detailed account of the analytical procedures can be found elsewhere<sup>10</sup>.

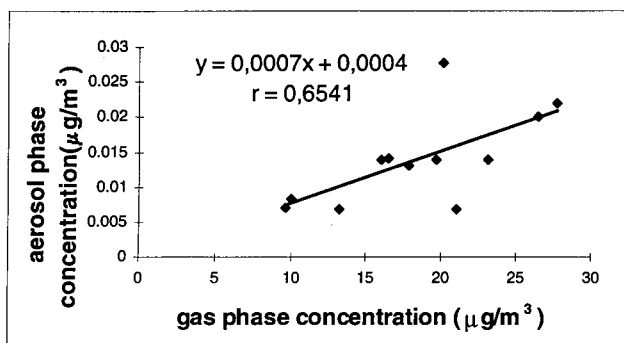
## Results and Discussion

Ambient levels of formaldehyde and acetaldehyde in the gas phase and associated with the aerosol phase in both sites studied are listed in Table 1. During the sampling period the formaldehyde and acetaldehyde concentrations in the aerosol phase ranged from 0.007 µg/m<sup>3</sup> to 0.232 µg/m<sup>3</sup> and 0.003 µg/m<sup>3</sup> to 0.089 µg/m<sup>3</sup>, respectively. These values are smaller than those measured in the gas phase, which were from 11.8 µg/m<sup>3</sup> to 109 µg/m<sup>3</sup> for formaldehyde and 2.81 µg/m<sup>3</sup> to 167 µg/m<sup>3</sup> for acetaldehyde. At the bus station, a site strongly influenced by diesel-fueled vehicles, the major aldehyde in the gas phase was formaldehyde, whereas inside the tunnel, which is representative of the vehicular pattern of the city of Salvador, acetaldehyde prevails. This is in agreement with previous data obtained in Rio de Janeiro by Tanner *et al.*<sup>2</sup>, and with measurements of aldehyde concentration in the exhaust emissions of ethanol fueled vehicles<sup>12,13</sup> in which it was found that formaldehyde and acetaldehyde comprised about 99% of the carbonyl compounds of exhaust, while acetaldehyde makes up between 88.3 and 99.3% of the total aldehydes determined.

**Table 1.** Formaldehyde and acetaldehyde concentrations ( $\mu\text{g}/\text{m}^3$ ) in the gas phase and aerosol phase.

Site	Formaldehyde		Acetaldehyde	
	Aerosol phase	Vapor phase	Aerosol phase	Vapor phase
bus station	0.0139	28.41	0.0417	12.50
	0.0139	19.66	0.0347	2.81
	0.0220	34.09	0.0514	14.77
	0.0278	24.72	0.0550	3.37
	0.0069	25.84	0.0278	10.11
	0.0069	16.29	0.0277	2.81
	0.0140	20.22	0.0350	5.62
	0.0139	24.16	0.0416	8.99
	0.0083	12.36	0.0330	10.67
	0.0071	11.80	0.0283	13.48
	0.0200	32.58	0.0347	21.91
0.0131	21.91	0.0392	13.48	
tunnel	0.152	92.38	0.054	167
	0.196	108	0.089	124
	0.232	99.2	0.071	126
	0.071	90.5	0.027	98.4

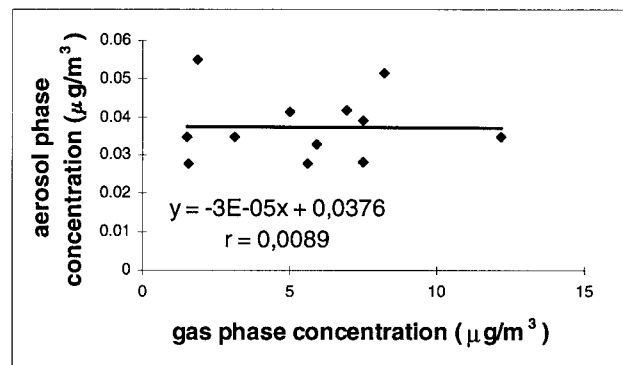
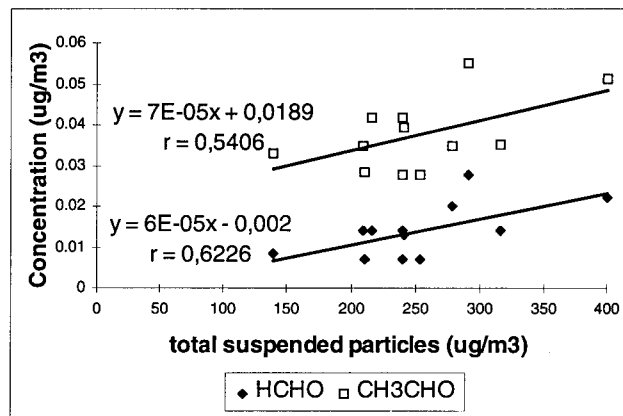
In the aerosol phase, in all samples collected at the bus station, acetaldehyde prevails. Formaldehyde is known to form adducts or condensation products with many substances, both organic and inorganic, one of the most important adducts being with  $\text{SO}_2$ , producing hydroxymethane sulfonic acid<sup>14</sup>. When formaldehyde is in this form it does not react with the DNPH solution. This may explain the lower values for formaldehyde, in the aerosol phase when compared to acetaldehyde, since the corresponding adduct with acetaldehyde is not as stable as that with formaldehyde<sup>14</sup>. Fig. 1 shows that there is a correlation ( $r = 0.6541$ ) between the formaldehyde concentrations in the gas phase

**Figure 1.** Correlation between the formaldehyde concentrations in the gas phase and the aerosol phase.

and the aerosol phase. However, this does not occur ( $r = 0.0089$ ) with acetaldehyde (Fig. 2). In the samples collected inside the tunnel the acetaldehyde levels in the aerosol phase were in the same range as those determined for the bus station site, but the formaldehyde levels were *ca.* ten times higher than those determined for the bus station site. Considering that the gas phase aldehyde concentrations inside the tunnel were much higher than at the bus station (Table 1), this could explain the formaldehyde enrichment, but we cannot explain the case of acetaldehyde in this manner. This and other aspects of carbonyl accumulation in particulate matter warrant further investigation.

Fig. 3 shows that both formaldehyde ( $r = 0.6226$ ) and acetaldehyde ( $r = 0.5406$ ) aerosol phase concentrations increase with the total suspended particle concentration. Considering that the filter area and the sampling flow rate were the same for all samples, the influence of possible sampling artifacts due to gas phase aldehyde adsorption on the filters<sup>9</sup> was minimal.

The aerosol phase/gas phase concentration ratios for both carbonyl compounds are lower than  $10^{-2}$ , so that more than 99% of the total aldehyde mass concentration is found in the gas phase, and less than 1% in the aerosol phase.

**Figure 2.** Correlation between the acetaldehyde concentrations in the gas phase and the aerosol phase.**Figure 3.** Correlation between formaldehyde and acetaldehyde concentrations and total suspended particle concentration.

**Table 2.** Estimated formaldehyde and acetaldehyde concentrations ( $\mu\text{g}/\text{m}^3$ ) in the aerosol droplet.

Site	HCHO	CH <sub>3</sub> CHO
	( $\mu\text{g}/\text{m}^3$ ) $\times 10^{-5}$	( $\mu\text{g}/\text{m}^3$ ) $\times 10^{-5}$
bus station	6.26	5.28
	3.78	1.04
	12.5	10.4
	6.61	1.73
	5.70	4.28
	3.79	1.25
	5.87	3.13
	4.80	3.42
	1.57	2.61
	2.28	5.00
	8.34	10.8
	4.85	5.73
	tunnel	115
91		270
120		420
76		220

This is in agreement with previous data obtained by Klippel and Warneck<sup>9</sup> and Grosjean<sup>3</sup>. These small aerosol phase concentrations appear to be much higher than those predicted on the basis of a simple equilibrium between the aqueous and gas phases. From the analysis of Klippel and Warneck<sup>9</sup> and Grosjean<sup>3</sup>, droplet carbonyl concentrations can be estimated from the relation

$$C_l = H C_g W$$

where  $C_l$  and  $C_g$  are the carbonyl concentrations in the aerosol droplet and in the gas phase, respectively,  $W$  is the mass concentration of water in the aerosol droplet, and  $H$  is the Henry's law coefficient for the carbonyl under investigation. In the case of formaldehyde and acetaldehyde,  $H = 7.51 \times 10^{-8} \text{ m}^3/\mu\text{g}$  and  $2.11 \times 10^{-7} \text{ m}^3/\mu\text{g}$ , respectively, at 25 °C<sup>15</sup>. Using the value assumed by Grosjean<sup>3</sup> for  $W$  (15% of the aerosol mass concentration) and the determined  $C_g$  concentrations, we were able to estimate the  $C_l$  concentrations (Table 2), which were *ca.* 1000 times less than the measured formaldehyde and acetaldehyde aerosol phase concentrations. This is in agreement with previous conclusions made by Grosjean<sup>3</sup>, in which the simple gas-aqueous droplet equilibrium does not fit these data. In addition to the various factors pointed out by Grosjean<sup>3</sup> to explain his observations, we believe that most of the formaldehyde and acetaldehyde found in the aerosol phase is directly adsorbed, since carbonyl compounds are polar and can easily interact with particles of condensed matter.

Furthermore, sampling artifacts may occur during filter sampling of ambient air when gaseous carbonyl compounds (for example) are adsorbed on the layer of deposited particulate matter. In this way, a sampling protocol which minimizes the sampling artifacts is under investigation in our laboratory, which involves the use of annular denuders coated with DNPH, followed by a filter for aerosol collection.

## Acknowledgments

This work was supported by the National Research Council of Brazil (CNPq). The authors thank Mauro Korn, André Esteves, Fátima Justo and Anselmo Elcana for help with the sampling, and Prof. Dr. José Oscar N. Reis for useful discussions. H.L.C.P was supported by a CAPES fellowship, and M.V.A. was supported by a CNPq fellowship.

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